

# Future Challenges in Heterogeneous Catalysis: Understanding Catalysts under Dynamic Reaction Conditions

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In the future, (electro-)chemical catalysts will have to be more tolerant towards a varying supply of energy and raw materials. This is mainly due to the fluctuating nature of renewable energies. For example, power-to-chemical processes require a shift from steady-state operation towards operation under dynamic reaction conditions. This brings along a number of demands for the design of both catalysts and reactors, because it is well-known that the structure of catalysts is very dynamic. However, in-depth studies of catalysts and catalytic reactors under such transient conditions have only started recently. This requires

studies and advances in the fields of 1) operando spectroscopy including time-resolved methods, 2) theory with predictive quality, 3) kinetic modelling, 4) design of catalysts by appropriate preparation concepts, and 5) novel/modular reactor designs. An intensive exchange between these scientific disciplines will enable a substantial gain of fundamental knowledge which is urgently required. This concept article highlights recent developments, challenges, and future directions for understanding catalysts under dynamic reaction conditions.

## 1. Introduction

At the sight of depleting fossil fuel reserves and facing increasing environmental problems connected to their continued usage,<sup>[1–4]</sup> novel strategies to power our society are presently being developed based on renewable energies. As for example planned within the German “Energiewende”,<sup>[5]</sup> renewable energies in combination with chemical energy conversion will play a crucial role in such future energy scenarios.<sup>[1–3, 6–10]</sup> A major challenge connected to the use of renewables like wind and solar power is that they provide energy in a highly fluctuating, time-dependent manner. Also, catalytic processes involved in the (electro-)chemical storage of electrical energy, as well as in the (subsequent) transformation to chemicals and fuels, will be necessarily subject to significant fluctuations unless sizeable

buffer systems are installed. This is schematically illustrated in Figure 1 and requires more decentralized plants with reactors that can be started up and ramped down depending on the availability of feedstocks from renewable resources. To complete the transition to a system entirely based on renewable energies, it is therefore essential to make chemical and electrochemical catalysts more tolerant against an alternating supply of energy and raw materials. The new boundary conditions contrast most of the former and current chemical processes that are continuously run in a single, more or less optimal operation window. Notwithstanding, even under steady-state conditions, dynamic changes are omnipresent in heterogeneous catalysis and electrocatalysis.<sup>[11–16]</sup>

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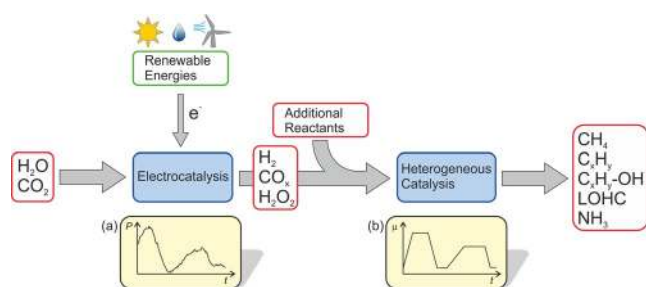
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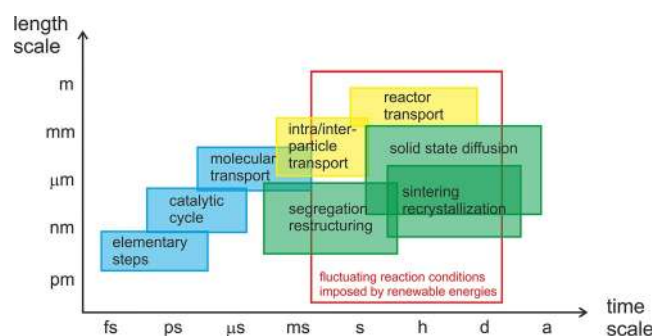
**Figure 1.** Schematic future scenario for power-to-chemicals processes demonstrating the importance of the development of more tolerant catalysts and processes a) time-dependent power production by wind energy in 48 h (source: Fraunhofer ISE, KW 9, 2015), b) smoothed profile of hydrogen by intermediate storage.

A fluctuating supply of energy and raw materials, as exemplarily given in Figure 1, affects both transport processes within the reactor or the porous catalyst materials and dynamic changes on the molecular catalyst level.<sup>[17–19]</sup> The latter are particularly demanding as changes of the performance of a catalyst, for example, as consequence of temperature or redox potential variations, are difficult to correlate to changes in the microscopic structure even under steady-state conditions. As one has to unravel catalyst structure, concentration and heat gradients in the reactor while the process is running (“operando”)<sup>[17,18,20–22]</sup> we have only recently begun to grasp these complex structure-function relationships. With the availability of new analytical methods, it is now possible to gain further insights into (electro-)catalytic systems and to obtain a deep molecular-level understanding even for variable reaction conditions.<sup>[12]</sup> Furthermore, theoretical approaches have evolved to an extent that they can now predict active sites and give input for kinetic modeling which will substantially contribute to understanding the complex relationships in dynamically operated systems.<sup>[23–25]</sup> Deriving such a microscopic understanding will be vital for adapting catalysts and chemical processes to the new boundary conditions.

Even though such a view on catalytic processes as derived from Figure 1 might appear rather new, changing reaction conditions have already been encountered in selected processes like fluid catalytic cracking<sup>[26]</sup> or exhaust gas catalysis.<sup>[27]</sup> In these cases, however, fluctuating reaction conditions are either used to restore the catalytic activity by circulating the catalyst periodically through a regenerator, or they are unintentional and a consequence of the respective engine operation as in the latter case. Research on process intensification by periodically fluctuating process conditions has shown great potential,<sup>[28]</sup> but has not yet been applied in an industrial setting. In contrast, in electrocatalysis, non-stationary conditions have been widely applied recently<sup>[29]</sup> and accelerated deactivation including dissolution of the electrocatalyst has been found.<sup>[16]</sup> Looking at catalytic systems under fluctuating reaction conditions as imposed by renewable energy sources will open up new possibilities for catalysis in general.

In this contribution, we outline the challenges for heterogeneous catalysis connected to such an increasingly fluctuating

supply of energy and raw materials. We will discuss possible strategies to correspondingly adapt existing catalysts and reactor concepts based on a thorough understanding of the microscopic processes occurring at the surfaces and in the bulk material of solid catalysts. Most recent pertinent developments in the field of heterogeneous catalysis will be described and illustrated by selected examples. Rather than providing a complete overview of the literature in this field, we aim to highlight the conceptual importance of considering dynamic reaction conditions when developing the catalytic systems of the future. The time scale considered lies between a few milliseconds, typical for time-dependent changes limited by mass and heat transfer, and a few hours, which is typical for restructuring, surface segregation, and the lower end of sintering processes (Figure 2).



**Figure 2.** Typical time and length scales relevant for dynamic processes in catalysis. Blue: molecular processes at the active site; green: processes involving solid state catalysts, yellow: transport processes of reactants and products. The time frame important for dynamic operation addressed in the present concept article (indicated with a red box) includes microscopic and macroscopic length scales.

## 2. Dynamic Reaction Conditions from a Catalysis Point of View

Today, most of the catalysts used in industrial processes are run at a certain operating point which is, if at all, mostly only altered if deactivation processes have to be compensated by gradually increasing the temperature. Yields and selectivities obtained under these static conditions usually correspond to optimal values found for the specific catalysts. As Figure 1 shows, this may be altered in future processes due to the altered framework conditions. One option would be to insert temporary storage capacities to provide a constant flow of reactants so that conventional catalysts and processes can be used. A more “innovative” approach which minimizes temporary storage capacities would be to redesign our catalysts and to develop more tolerant chemical processes. This poses, however, the following questions: What are the effects of changing reaction conditions to the catalyst on a molecular level? What is the time scale and can we exploit changes in the redox potential to create more active and kinetically stable phases? Can we minimize or even completely omit additional storage tanks by optimizing our catalysts to make them operational also under variable load, feed composition or temperature? Is a smart reactor, cell and process design able to minimize the

negative consequences of fluctuating reaction conditions to the catalyst?

In principle, subjecting catalysts to fluctuating reaction conditions is not a new concept in the field of chemical reaction engineering: Considerable research efforts have been devoted to the periodic operation of chemical reactors motivated, e.g., by the expectation that the nonlinearity of chemical kinetics and the interaction of heat and mass transport with chemical kinetics may cause synergistic effects on the effective reaction rate under certain circumstances.<sup>[28]</sup> In particular, periodic operation refers to a technique which aims at enhancing the performance of a catalytic reactor (which can for example, be measured as conversion, product yield, selectivity to a desired product or catalyst lifetime) by periodically manipulating the reactor input variables such as temperature or composition, pressure or flow rate of the reactor feed. Several results demonstrate the potential of such periodically operated reactors: For example, a 1000-fold increase in the reaction rate of a Ru catalyst in ammonia synthesis was found when cycling rapidly between H<sub>2</sub> and N<sub>2</sub>,<sup>[30]</sup> or the finding that the catalyst lifetimes of Cu-based water–gas shift catalysts were extended by multi-step composition and temperature cycles.<sup>[31]</sup> However, industrial applications of such concepts are still scarce.<sup>[32,33]</sup> According to Stankiewicz et al.<sup>[33]</sup> this is connected to the lack of basic understanding of the relevant effects which hampers a reliable and safe scale-up. Apart from that, difficulties such as a seemingly more complicated control of the process, heat integration and necessary additional investments are encountered when integrating periodic operation into a plant designed for steady-state operation.<sup>[33]</sup> Silveston and Hudgins provide a comprehensive summary on periodic operation of chemical reactors.<sup>[28]</sup>

An example for an industrial process with a catalyst that encounters varying reaction conditions is fluid catalytic cracking. The catalyst is periodically regenerated by passing through a regenerator to burn off coke depositions.<sup>[26]</sup> In automotive exhaust gas catalysis and automotive fuel cells, strongly changing reaction atmospheres are an integral part of the everyday challenges catalysts have to deal with, as for example, start-up, acceleration, deceleration or idling induce different air-to-fuel ratios, engine temperatures and flow rates.<sup>[34]</sup> Nevertheless, especially for stoichiometrically operated gasoline engines, the composition of the exhaust gas is usually held within a narrow range around the stoichiometric air-to-fuel ratio by means of a  $\lambda$ -sensor. Sometimes, oscillations in the activity occur, for example, for CO-oxidation and the oxygen-to-fuel ratio varies slightly, which is equalized by ceria and predictive control mechanisms.<sup>[35]</sup> Sometimes, like in the NO<sub>x</sub>-storage-reduction concept, the exhaust-gas stream is changed deliberately, that is, during the lean phase (typical exhaust gas from diesel engines, oxygen excess) NO<sub>x</sub> is stored and subsequently reduced during a small time window of a rich phase (hydrocarbons added). Changing the reaction atmosphere has also been exploited for improving the catalyst lifetime: In so-called “intelligent catalysts”, the oxidation of Pd nanoparticles was used to incorporate Pd into a perovskite lattice (e.g. Pd and LaFeO<sub>3</sub> to LaFe<sub>0.95</sub>Pd<sub>0.05</sub>O<sub>3</sub>).<sup>[36,37]</sup> Under reducing conditions Pd moves back

to the surface inducing a self-regeneration of the catalyst since the metal particles are effectively redispersed on the surface. For further information on such concepts in automotive exhaust gas emission control the reader is referred to corresponding reviews.<sup>[38,39]</sup> In dynamically operated fuel cells, humidification and CO impurities can have a strong impact on local catalyst state and can even lead to oscillations and chaotic behavior,<sup>[40]</sup> which might be detrimental to catalyst or cell life time. Also electrolyzers show strong changes of catalyst state and even dissolution during dynamic operation.<sup>[41]</sup>

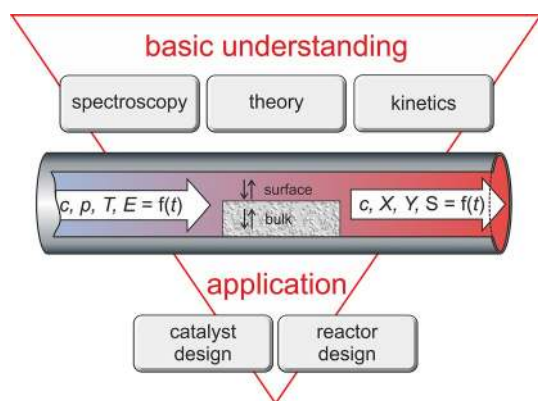
Apart from very few exceptions, industrial processes have so far mostly not been regarded in the light of dynamic reaction conditions relevant for energy storage applications. Even more unsatisfactorily, the catalyst itself has until now mostly been simplified as much as possible in kinetic rate equations, also in most of the cases described above. As the microstructure of the catalyst and, therefore, the exposed surface sites are strongly dependent on the environment (temperature, pressure, chemical potential, concentrations of the reactants), the catalytic performance will vary depending on the local reaction conditions. This requires both the development of a fundamental understanding at an atomic level and its integration into the theoretical and kinetic description of the catalyst under fluctuating conditions. Connected to this approach are the following two new trains of thought:

- 1) Researchers have not only to discover the optimum reaction conditions for a given catalyst, but also have to design a catalyst to act well under varying conditions (averaged optimum).
- 2) The kinetics should be based on reaction sites that can vary and not on static ones as observed under steady-state conditions.

Only through a combined effort of theory and experiment we will be able to get a fundamental understanding of catalysts at their atomic level and to deal with this multi-layered problem: Spectroscopy, theoretical understanding and kinetic modelling of state-of-the-art materials have to work hand-in-hand and with the mutual aim of understanding the catalyst at its atomic level in relation to the scale of the particle and the reactor itself. The knowledge generated from this holistic approach has then to be implemented into the design of novel materials and appropriate reactor concepts to tackle the future challenges (Figure 3). This approach is not only important for energy-storage processes, but in general for reactors and catalysts operated under dynamic conditions. In the following chapters, the challenges in the different disciplines are elaborated before highlighting future perspectives of dynamic operation modes of chemical reactors.

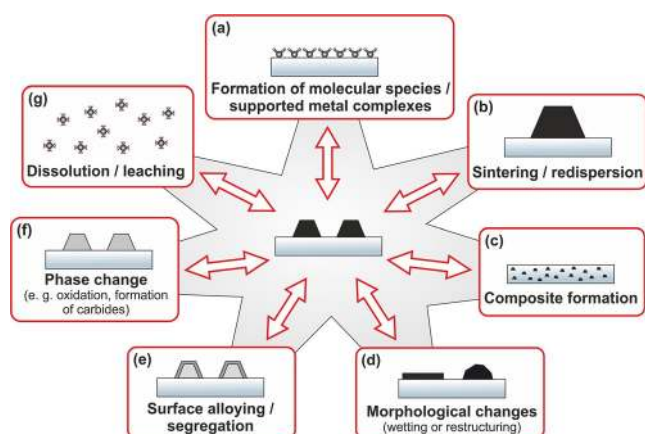
### 3. Snapshots on Working Catalysts: Case Studies Unravelling Structural Dynamics

Recent detailed insights into the structure-function relationships of heterogeneous catalysts lead increasingly to the conclusion that catalysts are by far not materials with static surface



**Figure 3.** For understanding catalysts under dynamic reaction conditions different scientific disciplines such as (operando) spectroscopy, theory and kinetic modelling have to work hand in hand in order to provide a basic understanding of the relevant processes at the catalyst surface and the bulk. In a second step, this knowledge can then be implemented into the design of novel materials and reactor concepts. Fluctuations of the incoming variables concentration ( $c$ ), pressure ( $p$ ), temperature ( $T$ ) and eventually electric potential ( $E$ ) influence the local state of the catalyst and thereby lead to variations of the product stream composition in the form of concentration ( $c$ ), conversion ( $X$ ), yield ( $Y$ ) and selectivity ( $S$ ) of a specific product.

and bulk structures. Instead, they are dynamic entities that may change their structure (e.g. morphology or composition of the surface) depending on the local reaction conditions in the reactor.<sup>[15,23,42,43]</sup> Usually, such changes on the atomic level also induce changes of the chemical properties. As can be seen by several examples given in Figure 4, structural changes of heterogeneous catalysts under reaction conditions are manifold.<sup>[15]</sup>



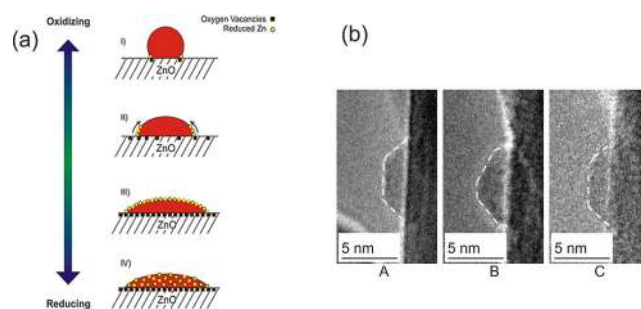
**Figure 4.** Examples for structural changes of supported metal nanoparticles resulting from changes of the environmental conditions (e.g. temperature, composition of the surrounding medium etc.).

For example, disruption of the metal particles to isolated organometallic centers (Figure 4a) may occur as observed in the case of partial oxidation of methane with Rh catalysts which form  $\text{Rh}^1(\text{CO})_2$  species under reaction conditions.<sup>[44,45]</sup> Sintering (Figure 4b) describes the agglomeration and gradual growth of nanoparticles. Usually this is connected to a decrease of the

catalytic activity of the catalyst which is a common problem in heterogeneous catalysis,<sup>[13,36,37,44]</sup> as well as in electrocatalysis.<sup>[16]</sup> Systems composed of several components often feature strong metal–support interactions. Changing redox potentials of the reaction mixtures may lead to differing adhesion between metal particles and the oxide support, which in turn might result in morphological changes (Figure 4d),<sup>[13,46]</sup> or decoration effects<sup>[47–50]</sup> on the metal surface. In extreme cases this may lead to composite formation (Figure 4c).<sup>[51]</sup>

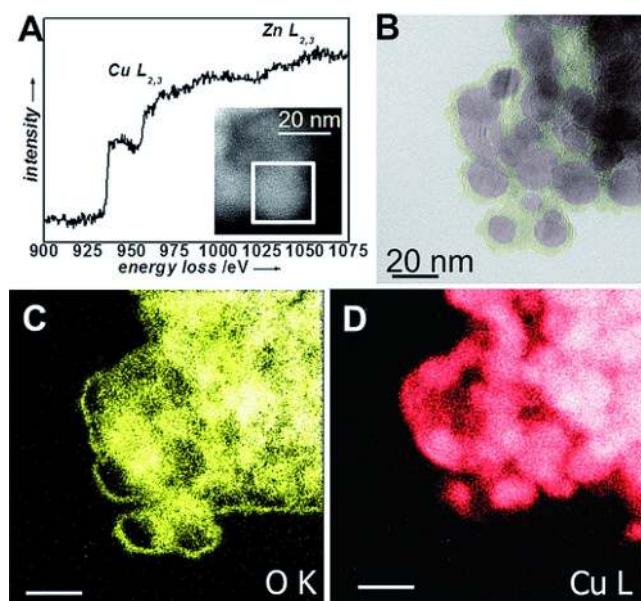
Likewise, bimetallic systems might show segregation of one metal on the surface depending on the reaction conditions (Figure 4e), which might lead to formation of core–shell structures as in the case of PdRh nanoparticles that show Rh segregation during NO oxidation.<sup>[52]</sup> Another example is the intermetallic compound  $\text{Pd}_2\text{Ga}$  for selective hydrogenations for which surface decomposition induced by oxygen impurities yields a Ga-depleted Pd phase and  $\text{Ga}_2\text{O}_3$  as active phases of the catalyst.<sup>[53]</sup> The phase change of a catalyst, for example, by oxidation<sup>[54,55]</sup> or by formation of carbides<sup>[56]</sup> (Figure 4f) is a frequently observed phenomenon in electro- and heterogeneous catalysis. Finally, the loss of active material by dissolution of metal particles (Figure 4g) is for example, encountered in electrocatalysis, in particular under non-stationary conditions.<sup>[16,41]</sup>

A prominent example for the response of metal nanoparticles on changes of the redox potential are the morphological changes of Cu/ZnO catalysts during the hydrogenation of  $\text{CO}_2$  to methanol in  $\text{CO}/\text{CO}_2/\text{H}_2$  mixtures with different redox potentials. With the help of operando EXAFS,<sup>[13]</sup> in situ IR spectroscopy,<sup>[57]</sup> and in situ electron microscopy<sup>[46]</sup> morphological changes induced by different reaction atmospheres could be detected (Figure 5). Formation of metallic Zn was recently evidenced by



**Figure 5.** a) Dynamic model for the change of Cu-particles in Cu/ZnO catalysts during the change of the reduction potential during methanol synthesis. Reprinted with permission from Ref. [13], Copyright 2000, Elsevier; b) TEM images showing the reversible shape change of a Cu nanocrystal. The same Cu nanocrystal is imaged at  $220^\circ\text{C}$  under A)  $\text{H}_2$  at 1.5 mbar, B)  $\text{H}_2/\text{H}_2\text{O}$  (3:1) at a total pressure of 1.5 mbar, and C)  $\text{H}_2$  at 1.5 mbar. Reprinted with permission from Ref. [46], Copyright 2002, AAAS.

titration and electron microscopy corroborated by DFT-calculations.<sup>[58]</sup> On the other hand, the formation of a metastable graphite-like ZnO overlayer was observed (Figure 6), which further exemplifies the complex interplay of Cu and ZnO and could be decisive for the extraordinary activity of the Cu/ZnO system.<sup>[47,58]</sup> The strong metal–support interactions crucially in-



**Figure 6.** Analysis of the overgrowth of ZnO on Cu-particles. A) STEM-EELS-spectrum of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> of the Cu L<sub>2,3</sub> and Zn L<sub>2,3</sub> edge of one single Cu nanoparticle. The inset denotes the corresponding HAADF-STEM image and the ROI from where the spectrum was collected. B) TEM image of the region where the EFTEM maps of C) and D) were recorded. C) and D) show oxygen K edge and copper L edge EFTEM maps of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, respectively. The scale bars in C) and D) are 20 nm. Reprinted with permission from Ref. [47], Copyright 2015, Wiley-VCH Verlag.

fluence the catalytic activity, which was also recently demonstrated by variation of the feed composition.<sup>[59]</sup>

These examples show clearly that structural changes provoked by the reaction conditions or interactions with reactants, intermediates, or products are an integral part of the catalyst's identity. Moreover, structural changes and catalytic activity are closely intertwined, which necessitates the simultaneous collection of spectroscopic and activity data to correlate both types of information.

#### 4. Advancing the Characterization Methods: Following Dynamics Operando

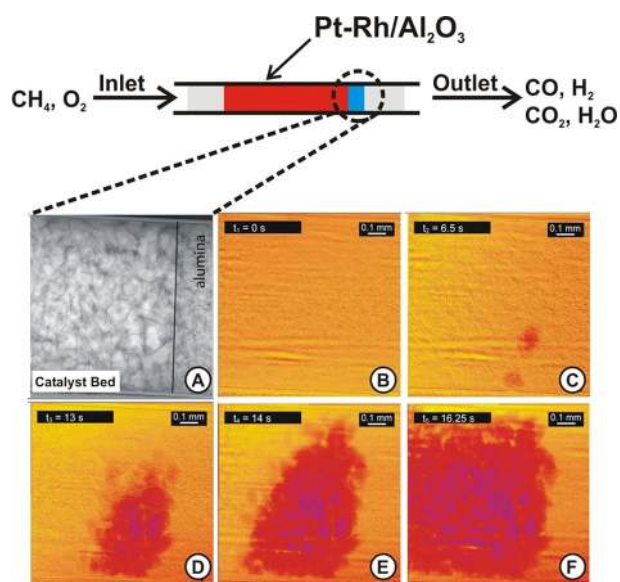
How can we further make the structural changes visible and simultaneously deduce their implications for the catalytic activity of the system? How fast are changes like those illustrated in Figures 4–6 and can more active phases be kinetically stabilized and regenerated? In this context the terms “in situ” and “operando” play a decisive role. In situ studies embrace experiments that are for example, performed during heating or cooling and in specific atmospheres. The term operando emphasizes that the spectroscopic study is conducted under reaction conditions close to those in a catalytic reactor allowing on-line catalytic or even kinetic studies. With the help of specially designed reaction cells enabling spectroscopic characterization of the catalyst under industrially relevant conditions and simultaneous monitoring of the catalytic performance, detailed structure-function relationships can be derived.<sup>[20–22,60]</sup> Here, also information obtained from the combination of multiple spectroscopic methods within the same cell are of high impor-

tance.<sup>[61–63]</sup> Such structure–function relationships are the basis for understanding the complex chemical processes and finally also for establishing a knowledge-based design of catalysts and reactors.

Nowadays a whole toolbox that essentially makes use of the interaction of electrons, neutrons and photons with the solid materials<sup>[64]</sup> is available for the investigation of heterogeneous catalysts. The field has recently received strong improvements which now allows for studying catalysts under transient reaction conditions. Firstly, model reactors have been developed which can operate closely to industrial operating conditions and which allow shining X-rays, IR, UV including laser light into the reactor. For example, reactors have been designed that allow for profiling temperature and concentration of species, while performing spectroscopy at the same time.<sup>[65,66]</sup> Even spatio–temporal studies are possible.<sup>[67,68]</sup> Secondly, microscopic tools have been developed further so that they can now provide atomic resolution even at atmospheric pressure (electron microscopy) or spatial resolution in the micrometer to the 10 nm scale including spectroscopic information (X-ray microscopic tools). Finally, surface sensitive techniques like XPS have been extended not only to provide information in vacuum, but also at elevated pressures or even in wet/liquid atmospheres. This allows insight into the surface structure complementary to bulk X-ray or infrared spectroscopic techniques. The advances in the field of catalyst characterization can be underlined by the following selected examples:

- 1) Good case studies can for example be found for hard X-ray techniques like X-ray absorption spectroscopy (XAS). XAS has become a valuable technique for the structural characterization of heterogeneous catalysts under reaction conditions as high-energy X-rays feature a large penetration depth.<sup>[69,70]</sup> Operando XAS has allowed analyzing dynamic changes during the oscillatory oxidation of CO<sup>[71]</sup> or partial oxidation of CH<sub>4</sub><sup>[72]</sup> uncovering in both cases strong changes in the oxidation state. Time resolution in the ms regime can be achieved using both dispersive EXAFS (DEXAFS, Turbo-XAS)<sup>[73]</sup> and quick-EXAFS (including a continuously scanning monochromator).<sup>[74]</sup> Using an X-ray camera even spatially and temporally resolved structure changes could be recorded, as exemplified in Figure 7. Furthermore, dynamic studies have been conducted dealing for example, with the in situ redispersion of Pt in an exhaust gas catalyst<sup>[75]</sup> during redox cycling or with reversible particle reconstructions of Cs-doped Ru-based Fischer–Tropsch catalysts during switching between CO/He and H<sub>2</sub>/He atmospheres.<sup>[76]</sup> Surface X-ray diffraction has further provided insight into reactions at the structure of defined nanoparticles on single crystal surfaces.<sup>[77]</sup>

Only recently, dynamic studies have been conducted in the field of energy storage, showing for example, that hydrogen drop-out had a strong effect on the structure of Ni-particles during CO<sub>2</sub>-methanation.<sup>[80]</sup> Moreover, stimulated changes of the gas atmosphere during so-called modulation-excitation spectroscopy<sup>[81,82]</sup> have received strong attention. Identifying transient states, they underlined that dynamic changes are not only of interest for applications, but also for fundamental mechanistic studies. Finally, the concept of hard X-ray tech-



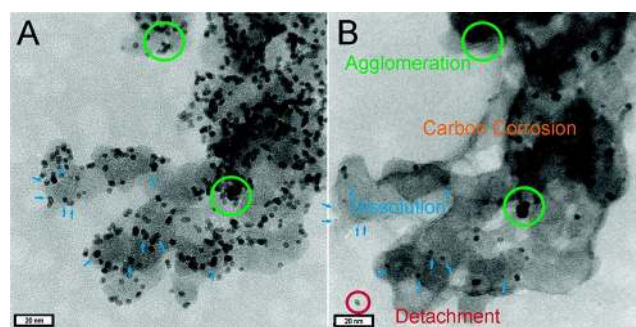
**Figure 7.** Spatio-temporal evolution of reduced Pt species during ignition of the catalytic partial oxidation of methane over 5%Pt-5%Rh/Al<sub>2</sub>O<sub>3</sub> (end of the evolution measured at 11586 eV close to the Pt L<sub>3</sub>-edge): A) X-ray absorption image recorded below the ignition temperature; B–F) Images recorded as a function of time. A reddish color indicates lower absorption and thus the formation of a reduced Pt-containing species. Adapted with permission from Ref. [78], Copyright 2009, American Chemical Society, and Ref. [79] with permission from the Royal Society of Chemistry.

niques has been extended to further photon-in/photon-out techniques (e.g. HERFD-XANES, X-ray emission techniques like V2C-XES),<sup>[83,84]</sup> and X-ray microscopic techniques.<sup>[18]</sup>

2) Within the last few years microscopic and tomographic methods on an atomic scale have made enormous progress. Especially electron microscopy has evolved to a true in situ method which can nowadays even be used for catalysts under gas atmospheres and at higher temperatures.<sup>[12,85–87]</sup> For this purpose, differentially pumped microscopes or systems making use of special window cells which confine the gas atmosphere are used. Furthermore, structural changes can now be followed by means of “identical location” (IL)-TEM and IL-tomography.<sup>[16,88]</sup> One example where IL-TEM was used to follow the effect of 3600 start–stop cycles on the catalyst structure is shown in Figure 8. Here, IL-TEM unraveled strong changes caused by the degradation cycles.

Prominent examples in which TEM was used to gain insights into dynamic structure changes of catalysts are the restructurings of Cu surfaces of a Cu/ZnO catalyst in different gas atmospheres (see also Figures 5 and 6),<sup>[46,47]</sup> carbon nanofiber growth on a Ni catalyst during methane decomposition,<sup>[14]</sup> and the refacetting of Pt nanocrystals during CO oxidation in a nanoreactor at 1 bar and at elevated temperatures.<sup>[89]</sup>

3) Traditional X-ray photoelectron spectroscopy (XPS) is restricted to ultra-high vacuum conditions, owing to the short mean free path of electrons in gas or condensed matter. This disadvantage has been successfully overcome using an ambient pressure cell (so-called ambient pressure (AP) XPS).<sup>[90]</sup> By utilizing energy tunable synchrotron X-rays for APXPS, the active catalyst surfaces and the interfaces between metal and



**Figure 8.** IL-TEM images after 0 (A) and after 3600 (B) degradation cycles of a Pt/C fuel cell catalyst. Green circles indicate agglomeration, the red circle shows a detached platinum particle, blue arrows point at platinum particles that decrease in size due to dissolution; additionally, massive changes in the support structure are observed (denoted “carbon corrosion”). Reprinted with permission from Ref. [16], Copyright 2012, American Chemical Society.

oxide support of catalysts can be explored including information on the reactivity using mass spectrometric analysis. Although the working gas pressure inside APXPS cells has mostly remained in the low mbar range,<sup>[90,91]</sup> recent developments in this field, however, show that operando XPS measurements under more realistic electrolysis conditions will become possible. The groups of Schlögl<sup>[92]</sup> and Nilsson<sup>[93]</sup> could, by means of XPS, unravel that during the electrochemical oxygen evolution reaction the degree of surface oxidation of platinum<sup>[92]</sup> and iridium oxide<sup>[93]</sup> electrodes change depending on the applied potential. In the XPS chamber a water pressure of 10<sup>−2</sup> mbar was achieved. An even more advanced setup<sup>[94]</sup> uses an electron-transparent Si<sub>3</sub>N<sub>4</sub> grid coated with bilayer graphene,<sup>[95]</sup> which separates the vacuum from a flow cell filled with liquid. The setup was recently also used for studying solids in a 1 bar reaction atmosphere including on-line monitoring of reaction products.<sup>[96]</sup>

These selected examples demonstrate that in situ and operando methods can nowadays provide spectroscopic information on the bulk and the surface in a highly time- and spatially resolved manner. This paves the way for investigating dynamic processes of catalytic materials.

## 5. Theory and Molecular Modelling: Understanding Catalysts under Dynamic Reaction Conditions

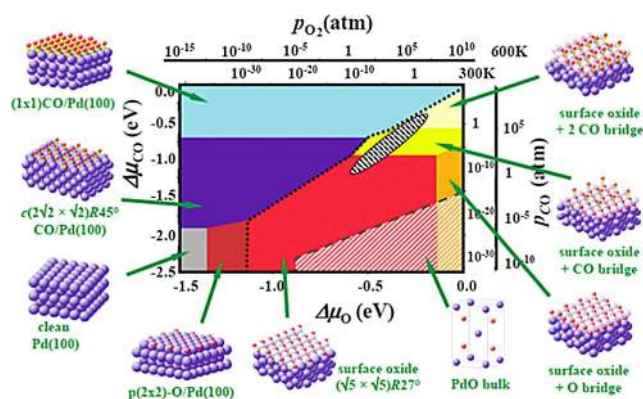
To understand the processes/changes of the catalyst state (bulk and surface) we do not only need to follow/record the variations with the help of spectroscopic methods. A theoretical description, preferentially with predictive quality, is equally required. For steady-state operation conditions molecular-level modelling and simulation has already taken up the role of such an increasingly valuable, if not indispensable partner in the quest for an atomic-scale understanding of catalytic function.<sup>[24,97,98]</sup> Corresponding approaches are predominantly based on first-principles electronic structure theory and density-functional theory (DFT), in particular, with selected aspects also treated on the level of (reactive) force fields. Central outcomes comprise spectroscopic signatures to support the inter-

pretation of experimental data and reaction energetics of elementary processes to aid the development of mechanistic models. Within the increased complexity of dynamic reaction conditions such independent, predictive-quality theoretical input will become ever more important. Fortunately, and due to the disparity of reactor and molecular time constants, cf. Figure 2, the entire methodology developed and continuously advanced for steady-state operation can equally be applied to dynamic reaction conditions—then focusing on snapshots of the evolving system.

The remaining central challenge is to come up with structural models for the presumed active sites as input to such calculations. Considering the morphological, compositional and structural changes induced by the reactive atmosphere as described in Section 3, the generation of a corresponding pool of candidate structures is already a daunting task for steady-state operation. It will not become easier for dynamic operation. At present, candidates are primarily generated by chemical intuition and available experimental information such as derived by methods in Section 4, to be iteratively refined and validated for example, through the comparison of computed and measured spectroscopic signatures. Valuable lines of research will aim to complement this with more automatized approaches, for instance relying on global geometry optimization.

Recent years have seen a rapidly increasing use of thermodynamic approaches to assess the stability of given candidate structures under realistic reaction conditions. In these approaches, termed *ab initio* thermodynamics in the context of heterogeneous catalysis<sup>[23,99]</sup> and computational hydrogen electrode in the context of electrocatalysis,<sup>[100,101]</sup> the surrounding gas or liquid phase is represented by reservoirs, which then allows to compare structures of differing composition within a grand-canonical framework. This leads to the prediction of thermodynamically stable (surface) phases either in form of phase diagrams as a function of the chemical potentials of the reactants or in form of Pourbaix diagrams as a function of pH and applied potential. Figure 9 illustrates this for a Pd model catalyst surface in environments representative of CO oxidation catalysis.<sup>[102,103]</sup> Note the closeness of the predicted transition temperatures and pressures inducing surface oxide formation (dashed line in Figure 9) to technological steady-state operation conditions. Corresponding diagrams have already made significant contributions towards an understanding of phase stability or reaction-induced phase transitions of working catalysts under steady-state operation. They will equally serve to discuss dynamic reaction conditions, most straightforwardly when the feed or potential changes imply a crossing of phase boundaries in the corresponding diagrams, that is, for instance a crossing of the dashed line in Figure 9. Major limitations to this approach are, of course, its thermodynamic nature and the concomitant inability to account for kinetic hindrances, the at present only indirect treatment of solvation effects, as well as the restriction of its predictive power to the pool of explicitly tested candidate structures.<sup>[23]</sup>

First-principles calculations for an established active site model and its interactions with possible reaction intermediates provide access to the binding energetics and a wealth of elec-



**Figure 9.** Surface phase diagram for a Pd(100) model catalyst in “constrained” thermodynamic equilibrium with an environment consisting of O<sub>2</sub> and CO. Phases involving the pristine metal termination are above the dotted line, phases involving the surface oxide are below the dotted line, while bulk-like PdO is stable at operation conditions below the dashed line. The dependence on the chemical potentials of O<sub>2</sub> and CO in the gas phase is translated into pressure scales at 300 and 600 K. The black hatched ellipse marks gas-phase conditions representative of technological CO oxidation catalysis, i.e., partial pressures of 1 atm and temperatures between 300 and 600 K. Adapted from Ref. [102]; available under the terms of the Creative Commons Attribution 3.0 License, Copyright 2007.

tronic structure information. These data often already afford valuable insight into structure–activity/selectivity relationships, and are increasingly used to establish descriptors of the catalytic function. The latter then form the basis for extended computational screenings of suitable catalyst materials.<sup>[104]</sup> Extending the energetic calculations to reaction barriers additionally allows to compute first-principles rate constants, currently almost exclusively within (harmonic) transition state theory.<sup>[97]</sup> The recent quantification of Brønsted–Evans–Polanyi and equivalent relations has been an important milestone in this respect.<sup>[105]</sup> Corresponding scaling relations allow to minimize the computationally intensive first-principles calculations, in particular of reaction barriers, and thereby to make first-principles rate constants much easier accessible. Over the last decade microkinetic models using or even entirely based on such first-principles data have correspondingly been devised for reaction networks of ever increasing complexity.<sup>[23,24,97,98]</sup> To date, all such first-principles microkinetic and computational screening work has focused on steady-state operation. The extension of corresponding concepts to dynamic reaction conditions is an exciting prospect that promises in depth mechanistic understanding and the extraction of simplified trend descriptions for the design of improved catalysts and process conditions alike.

## 6. Multi-Scale and Kinetic Modelling: From the Micro to the Macro Scale

Kinetic modeling of heterogeneously catalyzed chemical or electrochemical reactions is a key tool to understand and optimize the behavior and performance of the corresponding surfaces, reactors, and cells.<sup>[25]</sup> Macroscopic models are already widely and successfully applied to steady state—and in elec-

trochemistry to dynamic operation<sup>[106]</sup>—though without taking into account changes of the state of the catalyst. As chemical reactors are usually operated in steady state, most kinetic models contain lumped kinetics ignoring elementary steps and dynamic behavior, but reproducing temperature and concentration dependence. Notable exceptions are dynamic models for catalytic converters for automotive applications,<sup>[107]</sup> where dynamic operation is considered normal. Recently, CO and CO<sub>2</sub> methanation have also been regarded in the light of dynamic operation.<sup>[108]</sup> Dynamic kinetic models are more widespread in electrocatalysis, as the corresponding systems, such as batteries, fuel cells, and electrolyzers, are frequently operated dynamically. Furthermore, owing to the still limited options for monitoring the electrode state, except by current and voltage, electrochemists apply a sophisticated set of dynamic electrochemical analysis methods for kinetic studies, such as impedance spectroscopy and nonlinear frequency response analysis, to gain more information. These measurements are increasingly used for kinetic modeling, comprising model and parameter identification and analysis.<sup>[106]</sup> Coupling them to simultaneous dynamic concentration monitoring by operando characterization techniques will further aid micro- and macrokinetic modeling, especially if the technique allows for quantifying concentration dynamically. This has been recently demonstrated by a differential electrochemical mass spectrometry (DEMS) study on dynamic CO oxidation on a porous Pt electrode: The chronoamperometric response and the CO<sub>2</sub> concentration at the surface of the porous electrode were detected quantitatively and in sub-second time steps; the corresponding macrokinetic model allowed for a quantitative parameter identification and a view into the dynamic concentration profile in the electrode.<sup>[109]</sup> The combination with quantitative operando surface monitoring techniques may in future allow also for kinetic model identification and validation including changes in catalyst or surface states.

Kinetic models traditionally are differential algebraic equation systems containing among others species balances accounting for reaction and sorption processes to model microkinetics and optionally transport processes to model macrokinetics. Even experimentally observed complex dynamics, for example, oscillatory or chaotic behavior and its relation to spatially distributed states, can be understood using such models.<sup>[40]</sup> The corresponding reaction and sorption kinetic constants are usually determined experimentally by using macroscopic reactors operated close to technically relevant conditions. Any temporal or spatial change of the state of the catalyst is usually neglected.

As an exciting and promising alternative to experimental parameterization kinetic models can be connected to the rapidly advancing field of molecular-level modeling. This allows obtaining independent information on reaction mechanisms and kinetics from first-principles calculations. Here, a wide range of synergies is perceivable. Thermodynamic data as described above allows integrating more detailed and reliable reaction mechanisms or activation energies. Furthermore, first-principles microkinetic or kinetic Monte Carlo (kMC) simulations yield information on kinetics, such as kinetic constants.<sup>[23]</sup> Presently,

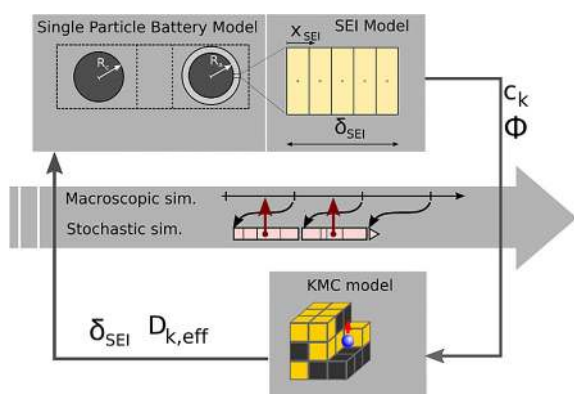
a major challenge<sup>[106]</sup> is that such molecular modeling is still largely restricted to or focused on ideal, well-ordered surfaces, whereas real catalyst surfaces have often a more heterogeneous, complex polycrystalline surface. The first-principles parameters thus deviate significantly from experimentally determined, effective parameters,<sup>[23,97,110]</sup> permitting direct usage in macroscopic models at best for general, but not quantitative studies. Systematic efforts to close this gap and to gain a better understanding of the interplay between microscopic processes and macroscopic behavior should not only be conducted starting from the molecular, microscopic side. Instead, a combined approach including also the scientific community dedicated to the macroscopic side, using for example, lumped or coarse grained kMC models and multiscale modeling,<sup>[111–113]</sup> should be pursued.

This leaves the final question on how to integrate surface changes into kinetic models. The macroscopic modeling methodology is in principle extendable to effectively embrace changes in catalyst state as shown in Figure 4 together with the corresponding, experimentally observed change in kinetics.<sup>[114]</sup> However, this would require additional, well-defined experiments with surface monitoring or molecular modeling. Degradation processes including oxidation, dissolution, growth, diffusion, delamination and even Ostwald ripening of catalyst and its support have already been integrated into macroscopic models using macroscopic rate equations.<sup>[111]</sup> However, most of these studies focus purely on steady-state operation, so modifying the models for dynamic operation is the next logical step. Also here, quantitative results require additional sophisticated and rapid surface monitoring techniques or molecular simulations.

A very exciting emerging field is to directly combine molecular-level modeling and macroscopic models to implement more first-principles knowledge and to study multiscale effects. A wide range of combinations with DFT and MC<sup>[111]</sup> or kMC<sup>[112,113]</sup> on the one hand and computational fluid dynamics or classical macroscopic or degradation models on the other hand is ready to be explored. Figure 10 illustrates with the example of a degrading Li ion battery the coupling of a macrokinetic cell model and a kMC-based degradation kinetic model for multiscale modeling. The degradation layer growth is determined by the complex reaction and sorption kinetic steps implemented in kMC and macroscopic boundary conditions such as concentration; growth is slowed down due to transport limitation through the degradation layer; the macroscopic part of the multiscale model predicts then the experimentally observed performance losses vs. time in cell voltage and capacity due to the degradation process.

Finally, it should be noted that modeling, identifying and analyzing the reaction, surface change and transport processes, as well as their complex interactions and dynamics requires also a systems view on chemical and electrochemical reactions and reactors. The already existing field of systems chemistry<sup>[115]</sup> may be extended and complemented by systems electrochemistry.





**Figure 10.** Multiscale model for a degrading Li ion battery: The macroscopic model contains a full battery cell model with mass and charge balances in electrolyte, electrode and degradation layer, whereas the KMC model contains the degradation kinetics with detailed sorption, reaction, surface diffusion processes and Li intercalation. The exchange of states and constants in each time step between the deterministic and stochastic model requires step size synchronization and filtering of KMC output.<sup>[113]</sup>

## 7. Rational Design of Catalysts and New Reactor Concepts

Apart from catalyst activity and selectivity, especially the life-time/stability is a key part that is to date mostly studied under static conditions. While for a long time a trial-and-error method was used to improve catalytic materials, we nowadays aim at a knowledge-based design. This comprises the design of the active phase based on structure-function relationships, a particle/pellet design with optimized heat and mass transport properties, and a reactor design optimizing fluid dynamics and heat transfer based on multi-scale modeling. Triggered by the new boundary conditions in the energy sector, the adaptation of the presently applied catalytic materials to dynamic reaction conditions including strategies for reactor design are expected to give an altered impetus to these efforts.

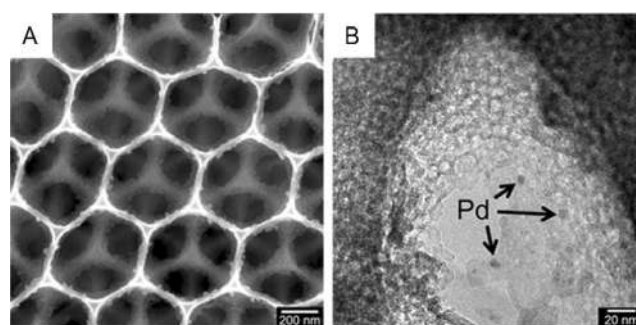
Although only scarcely studied, alternating reaction conditions are usually believed to result in faster catalyst degradation. In case of Cu-particles on Zn, rapid sintering owing to a change of the redox potentials was observed.<sup>[13]</sup> Similarly, an accelerated deactivation of Ni-catalysts by fast bulk oxidation was found in the methanation of CO<sub>2</sub> after removal of H<sub>2</sub> from a H<sub>2</sub>/CO<sub>2</sub> (4:1) gas stream.<sup>[80]</sup> In electrocatalysis, to identify the degradation process in fuel cell catalysts, typically several 10 000 start-stop cycles are performed and the resulting changes in the properties of the catalysts are subsequently analyzed.<sup>[116]</sup> Several coupled degradation mechanisms, such as dissolution, agglomeration, and detachment of particles, as well as corrosion of the support (see also Figure 8) were found for Pt-supported catalysts.<sup>[116]</sup>

However, dynamic reaction conditions do not necessarily have a negative influence on the catalyst performance. They can also lead to the formation of an active phase. For methanol synthesis over Cu/ZnO catalysts for example, it was observed that during switching from CO<sub>2</sub>/CO/H<sub>2</sub> to CO<sub>2</sub>-free synthesis gas and back, the methanol yield can be enhanced for several hours.<sup>[117]</sup> This effect can be directly utilized for the for-

mation of active phases during the time period of a low-load regime.

Hence, to tackle the challenges lying ahead, a fundamental understanding of the processes taking place at the catalyst's surface and bulk material needs to be gained and then translated into the design of novel materials. For this purpose, suitable model catalysts have to be selected and thoroughly examined by spectroscopic methods. As demonstrated in the corresponding sections, theory and modelling approaches can then provide valuable information on electronic and structural effects which finally allow designing improved catalyst candidates.<sup>[24,104]</sup>

To ensure catalyst stability under dynamic reaction conditions, special concepts for catalyst synthesis have to be targeted with respect to the length scales of atoms, nanoparticles, and catalyst particles. Strategies such as soft templating and colloidal nanoparticle synthesis provide exact control over the support's pore structure and the size of active particles, respectively (Figure 11).<sup>[118]</sup> Catalyst supports can be also modified by



**Figure 11.** A) SEM and B) TEM images of a hierarchically porous Pd/TiO<sub>2</sub> catalytic coating consisting of size controlled Pd nanoparticles derived from a colloidal synthesis. The nanoparticles were incorporated into the pore system of a hierarchically meso-macro porous TiO<sub>2</sub> obtained via dual pore templating with PMMA latex and micelles of Pluronic F127. The catalyst provides high activity and selectivity in the hydrogenation of butadiene. Reprinted with permission from Ref. [118], Copyright 2012, American Chemical Society.

selective introduction of heteroatoms modifying the redox-and, hence, the corrosion properties of the catalysts. By changing the interaction between support and active metal species, the latter can be stabilized.<sup>[119]</sup> For the reverse water-gas shift (RWGS) reaction, Cu-based catalysts that are known to suffer from sintering when operated at elevated temperatures can be stabilized by promoters such as Fe.<sup>[120]</sup> Stabilizing effects can also be achieved by specific control of the morphology of the support. Prominent examples are Ni-nanoparticles supported on ZrO<sub>2</sub> with high specific surface area and porosity. These highly porous supports may increase the stability of the catalyst against coking at temperatures above 800 °C in the dry reforming of methane.<sup>[121]</sup> In another approach, Pt-based nanoparticles were specifically deposited in the mesopore system of a support<sup>[122]</sup> or within graphitized carbon hollow spheres.<sup>[123]</sup> The incorporation of nanostructured, bifunctional Co-particles into a zeolite matrix resulted in an increased stability under operating conditions of the Fischer-Tropsch syn-

thesis attributed to reduced mobility due to pore confinement effects.<sup>[124]</sup> Analogously, stabilization by nano-confinement has been observed for Pt-nanoparticles.<sup>[125]</sup>

Confinement via encapsulation as one possible strategy for catalyst design also works for electrochemical systems.<sup>[126]</sup> Galeano et al.<sup>[123]</sup> reported that AuPt@C yolk-shell materials showed strongly enhanced stability in repeated fuel cell start-stop cycles. Other approaches to the design of electrocatalysts with enhanced stability employ bimetallic nanoparticles, often realized as core-shell architecture.<sup>[127,128]</sup> The second metal introduced into these systems serves either as a sacrificial phase,<sup>[129]</sup> or modifies the electronic structure of the active metal in a way that the oxidation of the metal and thus its dissolution is shifted to higher potentials.<sup>[127]</sup> Other design options include the exact control of size and size distribution of the active particles. Strasser's group reported that small Pt particles are more susceptible to electrochemical dissolution and should thus be avoided in order to obtain stable catalysts.<sup>[128]</sup>

All presented design approaches have in common that they require a significant amount of understanding for both, the underlying catalyst degradation mechanisms, as well as mechanisms of pore and particle formation during catalyst synthesis. A deeper understanding must therefore be an integral part of new approaches to design improved catalysts. This includes in particular transient concentration profiles under fluctuating operation conditions,<sup>[130]</sup> as well as synthesis methods with improved structural control over pore systems<sup>[131,132]</sup> and particle properties.<sup>[132,133]</sup>

As already outlined in Section 2, reactor design also offers various opportunities regarding non-stationary operation. At the same time, there is a strong link between catalyst and reactor design. The latter has to provide appropriate local conditions for the catalyst to achieve high selectivity, high reaction rate, and a long lifetime. Catalyst deactivation is one of the major factors, with fluid catalytic cracking performed in riser-regenerator systems being the most prominent example. Providing or removing the reaction heat efficiently and guaranteeing an appropriate residence-time distribution under highly variable throughput are further challenges in reactor design. In this respect, reactor systems based on microchannel process technology offer many advantages.<sup>[134]</sup> The modular concept allows us to bypass one or several modules if the feed flow rate is low. The extraordinarily high heat-transfer performance enables excellent control of the reaction temperature, particularly if thin catalyst coatings on metallic substrates are used. This also allows quick startup or shutdown of units or maintaining the temperature of modules switched to idle for ensuring a high energetic efficiency of the overall plant. This strength of microchannel reactors has been demonstrated, e.g., in studies on forced periodic temperature oscillation<sup>[135,136]</sup> and pulsed activation of catalytic reactions.<sup>[137]</sup>

Temperature cycling can further improve the average reaction rate due to the nonlinearity of the chemical kinetics. Additionally, direct beneficial effects may be observed such as desorption of adsorbates blocking the surface. For disturbing adsorbates a performance increase may also be achieved by periodic regeneration of the catalyst via dynamic changes of the

reactant concentration or the feed load. This has been shown recently for electrochemical cells.<sup>[106]</sup> The resulting reducing or oxidizing conditions reactivate the catalyst surface either by oxidation or reduction of the catalyst or by desorption of adsorbates. This strategy is applied in practice, e.g., in direct methanol fuel cells. More detailed understanding of processes in electrolytic cells would enable and better exploit a directed use of dynamic operation.

Another approach in reactor design for coping with imposed variable-flow rates or feed compositions is to provide a system capable of damping out the fluctuations, e.g., due to a high heat capacity or high capacity for accommodating the reactants. One example is the use of slurry bubble column reactors for methanation.<sup>[138]</sup> In a related study the potential of tubular packed-bed reactors for CO<sub>2</sub> hydrogenation to C<sub>2</sub>-C<sub>4</sub> hydrocarbons under variable feed conditions was analyzed both by experiment and simulation.<sup>[139]</sup> Nevertheless, studies addressing the dynamic behavior of catalytic reactors and solid (electro-) catalysts for synthesis of chemical energy carriers remain largely underrepresented, and also a connection to the state of the catalyst in different places inside the reactor under such conditions is yet to be made. To tackle this, more work is needed in particular concerning the development of advanced laboratory reactor systems including catalysts, e.g., by combining X-ray<sup>[140]</sup> and optical<sup>[141]</sup> in situ spectroscopy, capillary techniques,<sup>[66]</sup> advanced methods for gas sampling, and effective approaches to reactor design and fabrication such as, e.g., microfabrication<sup>[142]</sup> and additive manufacturing (3D printing).<sup>[143]</sup>

## 8. Perspectives: New Catalytic Opportunities During Dynamic Operation

Besides the integration of flexible, modular, decentralized catalytic reactors, dynamic operation of reactors will be a key element in future energy storage technologies. Hardly any systematic research on the catalyst properties including structure and texture under such dynamic operation conditions has been conducted, except for recent studies in electrocatalysis. We have to catch up on these omissions. More recently, the boundary conditions are better than ever before because many tools to study and understand catalysts in detail have been developed and tremendous progress has been achieved in rational catalyst design and the design of (micro-)reactors. Several case studies already pave the way on how to analyze the extremely dynamic structures. The concept of investigating catalysts under forced dynamic conditions may be very rewarding, not only as it promises to gain more fundamental insights into the catalyst, but also as the gained knowledge may be exploited in other research areas like exhaust gas catalysis, selective oxidation reactions, fuel cells, batteries, or photocatalytic devices.

The challenges in the different scientific disciplines with respect to dynamic operation (Figure 3) are manifold: The spectroscopic and microscopic methods need to be further improved to provide surface and bulk structural information as well as gas phase concentrations in a spatially and time-resolved manner (recall also Figure 7). Moreover, molecular and

kinetic (multiscale) modeling will provide additional insight to rationalize changes of reactors and catalysts under dynamic conditions. A particular challenge is the identification of the different active catalytic centers, depending on the reaction conditions and the kinetics of the transformation from the more active to the less active (but thermodynamically more stable) state. Finally, molecular modeling needs to become capable of predicting the surface structure as a function of the dynamically changing reaction atmosphere, as this will then be the basis for the kinetic and multiscale modeling. Dynamic system analysis allows further understanding of the complex dynamic interaction and self-organization of processes and catalyst surfaces. Furthermore, the concepts for catalyst stabilization, e.g., by confinement effects, core-shell particles or strong metal-support interactions, which may be exploited under rationally adjusted reaction conditions, need to be developed further, especially for the purpose of dynamic operation. All these topics are interlinked with reactor design, both on the systems level enabling an improved understanding of all relevant phenomena (in situ/operando cells, advanced reactors for kinetic studies, etc.) and for eventually implementing the new concepts on a technical scale.

As the state of the art in the different areas shows, there is a huge potential to further develop the concept of rational reactor and catalyst design for dynamic operation conditions. This will result in an improved design of catalytic processes which are compatible with the demands of our changing energy sector. To achieve this ultimate goal, scientists from the different scientific disciplines (Figure 3) need to work hand in hand. Only this will allow for a knowledge-based design of new-generation catalysts and an optimal reactor design applicable for or even exploiting dynamic reaction conditions.

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