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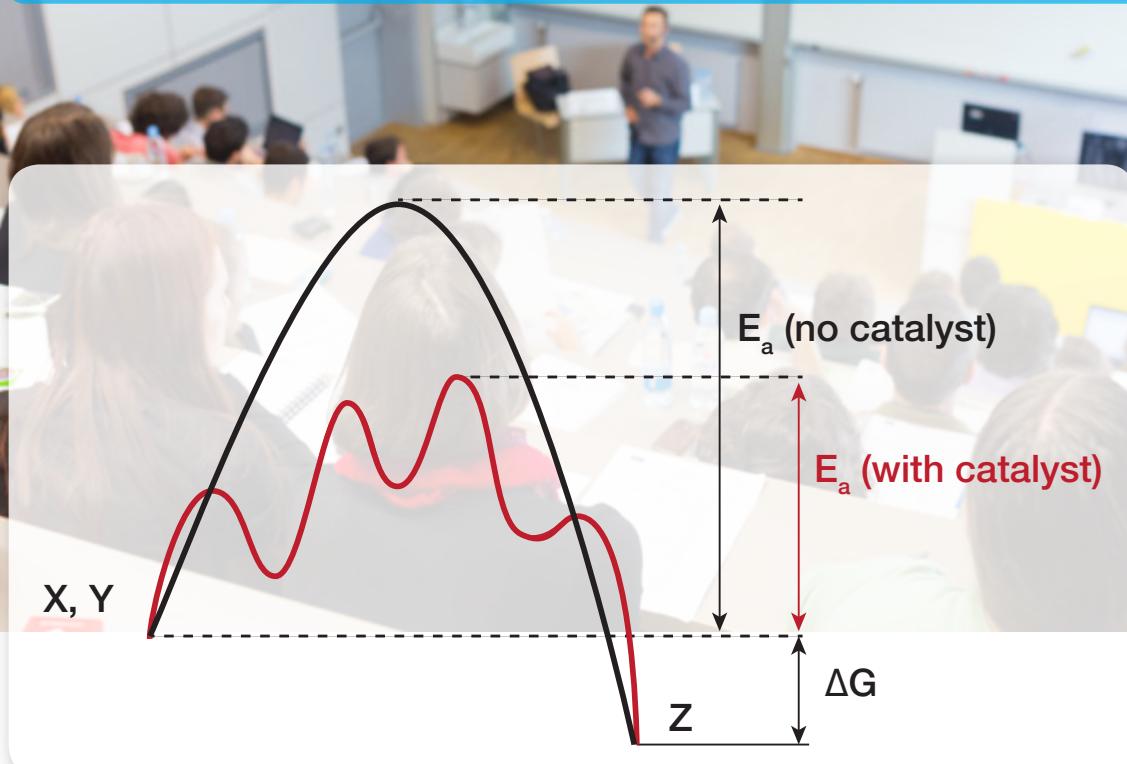
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# Key Topic Collection for Catalysis Teaching

## (Lehrprofil Katalyse)



**GECATS**  
GERMAN  
CATALYSIS  
SOCIETY



## TABLE OF CONTENTS

<b>1</b>	<b>Introduction</b>	<b>3</b>
<b>2</b>	<b>Implementation as Lecture Series</b>	<b>4</b>
2.1	Master of Science Courses	4
2.2	Doctoral and Postdoctoral Training Courses	4
<b>3</b>	<b>Fundamentals of Catalysis</b>	<b>5</b>
3.1	Underlying Concept	5
3.2	General Aspects	5
3.3	Nature of Catalysis	5
3.4	Stoichiometric vs. Catalyzed Reactions	5
3.5	Fundamentals of Catalysis	5
3.6	Activation Energy	6
3.7	Catalytic Cycle	6
3.8	Classification of Catalysis	6
3.9	Education in Catalysis in the Course of Time	6
3.10	History of Catalysis	6
<b>4</b>	<b>Kinetics and Elementary Steps</b>	<b>7</b>
<b>5</b>	<b>Testing of Catalysts</b>	<b>9</b>
5.1	Testing of Catalyst Properties	9
5.2	Approaches for Rapid Catalyst Performance Assessment: High Throughput Approaches	9
<b>6</b>	<b>Characterization of Catalysts</b>	<b>11</b>
6.1	Introduction	11
6.2	Characterization of the Microscopic Structure of Solid Catalysts	11
6.3	Characterization of the Microscopic Structure of Solid Catalysts	12
6.4	Deeper Understanding: Single Crystal Surfaces and In Situ/ Operando Studies	13
6.5	Appendix	14
<b>7</b>	<b>Computational Catalysis</b>	<b>15</b>
<b>8</b>	<b>Reaction and Process Engineering</b>	<b>16</b>
8.1	Introduction	16
8.2	Heat and Mass Transport Phenomena	16
8.3	Tailored Reactor and Process Concepts	16
8.4	Aspects of Industrial Catalysis	17

## TABLE OF CONTENTS

<b>9</b>	<b>Types/Classes of Catalysts</b>	<b>18</b>
9.1	Catalysis on Surfaces	18
9.1.1	Principles and Definitions	18
9.1.2	Mechanisms	18
9.1.3	Classification	18
9.1.4	Preparation of Solid Catalysts	19
9.1.5	Characterization of Solid Catalysts	19
9.1.6	Examples from Industrial Application	19
9.2	Molecular Catalysis	20
9.2.1	Principles and Definitions	20
9.2.2	Mechanisms	20
9.2.3	Classification	21
9.2.4	Preparation	21
9.2.5	Characterization	21
9.2.6	Examples	22
9.3	Biocatalysis	23
9.3.1	Principles and Definitions	23
9.3.2	Mechanisms	23
9.3.3	Classification	23
9.3.4	Preparation	23
9.3.5	Characterization Through Performance Data	24
9.3.6	Examples	24
9.4	Photo-, Electro- and Multicatalysis	25
9.4.1	Introduction	25
9.4.2	Photocatalysis	25
9.4.3	Electrocatalysis	25
9.4.4	Synergistic/Dual/Multi Catalysis	26
<b>10</b>	<b>What's Next?</b>	<b>28</b>
	<b>Imprint</b>	<b>33</b>

# 1 Introduction

The importance of catalysis is reflected by the overall economic impact on industry and society. This socio-economic impact of catalysis has - since the early days of establishment of industrial catalysis - been based on intensive efforts in research and development and on efforts driven by academia in teaching the scientific basis of catalysis. This document should be taken as a recommendation by GeCatS on how the scientific basis of catalysis can be presented in contemporary education. It is formulated in the format of a collection of key topics in the various areas of fundamental and applied catalysis. Catalysis as a scientific and technical topic is largely interdisciplinary and covers largely diverse areas most of which have the right to stand as disciplines of their own. As the current “teaching profile” aims at a comprehensive overview of the field rather than a thorough coverage of details, the contents of the subchapters had to be focused, but still allow representing the whole field within a reasonable framework. The present key topic collection is also an attempt to provide a guideline on how to unify common concepts in catalysis under one roof and connect scientific fundamentals with industrial applications. Moreover, it attempts to relate to the complete value chain based on and generated by the application of catalysis.

The focal point of this teaching profile is put on the catalyst as a core enabler and catalysis as a phenomenon. It is structured from the physico-chemical basis to the final industrial applications. As a side spin of this structure, chemical value chains and the virtue of catalysis in conjunction with these are also discussed.

The target groups of this key topic collection are lecturers in the field of catalysis active in teaching students holding at least a bachelor´s degree, i.e., graduates and post-graduates. Thus, the contents of this collection can be used in master-of-science courses as well as in doctoral and postdoctoral training programs. Specific target groups of lecturers are those holding comprehensive courses in the field of catalysis similar to the “Lehrverbünde” of GeCatS. From a topical point of view, the content of these key topics are intended not only to be suitable for chemists, physicists or chemical engineers, but can easily be adapted for students with different study areas.

Therefore, this document is organized into subchapters starting from a recommendation for implementing the key topics in modern catalysis education in a lecture format on the master-of-science and on the doctoral and postdoctoral, i.e., graduate, course level, respectively. Then, an introduction to the fundamentals of catalysis and to the molecular or atomistic view on elementary steps and kinetics relevant for all types of catalysis follows. After a chapter on characterization both with respect to the catalysts as materials, also under working conditions, and with respect to the methods of catalyst testing, key topics in computational catalysis and reaction and process engineering are presented. Within the subchapters on catalysis on surfaces, molecular catalysis, biocatalysis and other fields, the specific definitions, mechanistic characteristics, classifications and preparation methods are treated. Prominent examples illustrating both the principles and important industrial applications of these classes of catalysis are also referred to in these subchapters. A concluding chapter outlines the future challenges for catalysis. At the end of the document, a list of references is given. The latter does not aim for completeness, but rather guide the reader to important literature for further reading and details.

GeCatS is of the opinion that a solid education in catalysis is the basis for well-trained researchers and a foundation of excellence in both research and development. Finally, a modern catalysis education, which is supported by the chemical industry, will also aid graduates in the transition from scientific education and training into a professional academic or industrial environment.

## 2 Implementation as Lecture Series

For implementation of the key topics treated in this collection as lecture series, a differentiation into fundamental and advanced levels of teaching is appropriate. Therefore, all chapters in this document are color coded with regard to their content in order to give a recommendation at which level of education the content should be treated. For simplicity two color-codes were chosen: blue for fundamental education and red for advanced levels.

### 2.1 Master of Science Courses

For catalysis teaching in master-of-science courses, at least two lecture series equivalent to at least 40 hours attendance and 80 hours self-study over one semester each are recommended. These should treat the fundamental aspects (blue color-code) and may be expanded by selected topics of the advanced-level topics (red color-code). The relations of the catalysis-oriented topics to other aspects of teaching on the master level, e.g., physical and computational chemistry, chemical technology and engineering, preparation, characterization and structural chemistry of molecular, solid and biocatalysts, should be comprehensively addressed. These courses could be complemented by practical courses for hands-on learning of the most important fundamentals of catalysis. A course of 30 hours attendance and 30 hours self-study is recommended.

Moreover, selected topics of this collection could be offered in the form of specialized and advanced teaching modules, e.g., catalytic kinetics, catalytic reaction engineering, catalyst preparation and characterization, catalysis on surfaces, photocatalysis, molecular or biocatalysis.

### 2.2 Doctoral and Postdoctoral Training Courses

In structured graduate education on the doctoral and post-doctoral level, integrated training courses such as the Teaching Clusters for Catalysis held by GeCatS (“Katalyse-Lehrverbünde”) offer a broad overview and deep insights into all aspects of modern catalysis. These courses support the development of academic and research skills, and ultimately aim to prepare the participants for a future career in industrial or academic catalysis research. The corresponding graduate programs cover all aspects of this key topic collection. The topical structure can directly follow the structure of the presented key topic collection. The courses may include specialized topics and case studies from the research areas of the local lecturers, and contributions of experts from industry. Also, the participants can, individually or in groups, prepare and discuss presentations (oral or posters) to deepen their knowledge on specialized and advanced fields of catalysis. The time frame for such training courses is recommended to be equivalent to at least 40 h attendance and 80 h self-study. The courses can be taught as topical one-day sessions over one semester or as a block (approx. one week).

# 3 Fundamentals of Catalysis

## 3.1 Underlying Concept

Catalysis is an important field for economy, ecology and society. Fundamental principles of catalysis should be taught, with the goal of forming the basis for the remaining “Key Topics in Catalysis Education”, which include the phenomenon of catalysis, the difference to stoichiometric reactions as well as the introduction of fundamental concepts in catalysis (see below). Special care has to be taken to introduce these general concepts applicable for all specific types of catalysis correctly, including their inherent underlying principles and limitations (e.g., TON or TOF in heterogeneous, homogeneous and biocatalysis). Prominent examples of deep scientific understanding and insights are used to illustrate the historic development of knowledge.

## 3.2 General Aspects

- » The economic importance of catalysis is one of the largest driving forces and motivation for research and development in the fields of fuels and chemicals production as well as in environmental catalysis. Catalysis forms the basis of numerous large-scale chemical productions and of fossil fuel treatment. Based on a company overview it can be demonstrated how industrial turnover depends on the efficiency of catalysis. Catalysis also contributes to the creation of value in the domain of fine chemicals synthesis and the synthesis of high value products like pharmaceuticals.
- » However, ecology is also of major importance in the above mentioned fields of application. The development of new or improved catalyst systems which are more efficient, e.g., the three-way catalyst for automotive off-gas treatment, leads to improvements such as waste reduction or cleaner products like desulfurization for fuels.
- » With the gained access to new chemicals and materials, including pharmaceuticals and fine chemicals, the standard of living may be raised and the societal importance of catalysis can be demonstrated.
- » Last but not least, the value of catalysis in academic research is to be stressed. By aiming to obtain a deeper understanding of the underlying phenomena of the processes involved, new ways for improvement of existing catalysts and the development of new compounds can be achieved.

## 3.3 Nature of Catalysis

The historic development of the definition of catalysis from Berzelius to Ostwald, including today's IUPAC definition should be explained. The concept of catalyst precursor vs. catalyst is clarified by looking into the material dynamics. A catalyst is part of the catalytic cycle, it has a changing nature but is not consumed in the process. Materials changes can be reversible or irreversible, though. Catalyst poisoning and deactivation need to be taught as important phenomena and the principle of catalyst regeneration as important measure that can be taken.

## 3.4 Stoichiometric vs. Catalyzed Reactions

An introduction of the discrimination between reaction types should be made (e.g., the use of hydrides for catalytic as well as stoichiometric reactions). The advantages of catalyzed reactions including higher atom efficiency, waste reduction, or energy saving need to be stressed. The lower running costs of catalysis in continuously operated reactors have to be contrasted with the higher investment due to research efforts, plant installation and the like.

## 3.5 Fundamentals of Catalysis

- » Thermodynamics for a given chemical reaction cannot be changed. In this context, the terms endergonic vs. exergonic reactions, state of equilibrium, equilibrium conversion, and Le Chatelier's principle have to be explained.
- » Catalysis is a kinetic phenomenon, change of activation energies as well as ad-/desorption and reaction rates are key to understanding the phenomenon catalysis.
- » The definitions of activity (meaning the reaction rate under specific conditions as a comparative measure), selectivity and stability have to be treated within this context.

### 3.6 Activation Energy

The decisive influence of activation energy for the formation of products on competing reaction pathways may be demonstrated. Control of activation energies is the key to selectivity control and accordingly, the tuning of activation energy is one of the central topics in catalysis. The aspects of rate-determining step, activation energy vs. apparent activation energy, the concept of early and late transition state, and mass and heat transport limitations need to be treated in the course of the lectures. A comparison of experimental and calculated (by density functional theory and quantum chemistry) values is to be included.

### 3.7 Catalytic Cycle

The general definition specifies the catalytic cycle as a closed cycle of a multistep reaction that involves a catalyst as key component of the chemical transformation. However, differences and similarities in the catalytic disciplines need to be pointed out regarding, e.g., heterogeneous and homogeneous catalysis, organometallic chemistry, biochemistry/biocatalysis as well as electro- and photocatalysis. Examples for catalytic cycles, e.g., Heck process, Wacker process, are given. This is the opportunity for an introduction of turnover number (TON) and turnover frequency (TOF), which are of reliable use in homogeneous catalysis, but with strong restrictions in heterogeneous catalysis. Adsorption – surface reaction – desorption vs. elementary steps in homogeneous catalysis (oxidative addition, reductive elimination etc.) have to be distinguished.

### 3.8 Classification of Catalysis

Catalytic cycles can be classified into redox catalysis comprising reduction and oxidation, acid and base catalysis. Michaelis-Menten kinetics and autocatalysis should also be discussed in this context.

### 3.9 Education in Catalysis in the Course of Time

A holistic approach to teach catalysis is advisable, stressing the interplay between chemistry, chemical engineering and materials science. This includes the mechanisms in heterogeneous catalysis (e.g., understanding and application of the Langmuir-Hinshelwood, the Eley-Rideal and the Mars van Krevelen mechanisms), in homogeneous catalysis (e.g., acid base catalysis, transition metal catalysis, organocatalysis) and biocatalysis as well as characterization methods.

### 3.10 History of Catalysis

- » concepts of catalysis (cf. Elizabeth Fulham, Jöns Jakob Berzelius, Eilhard Mitscherlich, Johann Wolfgang Döbereiner, Humphry Davy, Wilhelm Ostwald);
- » industrial catalytic processes (e.g., ammonia synthesis, Fischer-Tropsch synthesis, olefin polymerization, ethylene chlorination, hydroformylation); petrochemistry (e.g., refining, upgrading, fluid catalytic cracking)

- A catalyst is a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis (IUPAC).
- The catalyst is both a reactant and product of the reaction (IUPAC).

## 4 Kinetics and Elementary Steps

Chemical kinetics is understood as the rate (speed) of a chemical process or a chemical reaction. Kinetic studies include the analysis of conditions affecting the rate, the understanding of reaction mechanisms and transition states, and mathematical modeling of the reaction rate. The derived kinetics are the basis for the design and optimization of any chemical reactor; it determines the reactor type, size, operational mode, shape of a catalyst and the operating conditions. The principles of kinetics apply for all types of catalysis and catalyzed reactions and are therefore understood as a unifying fundamental topic in the context of teaching. In the teaching it should be stressed that elementary reaction steps are the link in kinetics between all disciplines (homogeneous, heterogeneous, biocatalysis, electrocatalysis), but differences lie in the fact that certain phenomena like film diffusion or adsorption on surfaces do only apply to certain types of catalysis (in the latter case heterogeneous and electrocatalysis).

The mechanism of any catalyzed reaction can be described by the cycle of elementary reaction steps. Such steps include the elementary steps of the respective chemical transformations, and depending on the type of catalysis phenomena like adsorption, surface diffusion, chemical transformations of adsorbed species, and desorption. The formulation of rates of the catalytic cycle as function of the microscopic conditions, i.e., concentrations, temperature and catalyst state, without any impact of heat- and mass-transfer is understood as microkinetics. It should be pointed out that especially in heterogeneous catalysis effects like surface diffusion, dissociation and reactions of certain reagents with surface and even bulk of the catalyst are also treated as *microkinetics*.

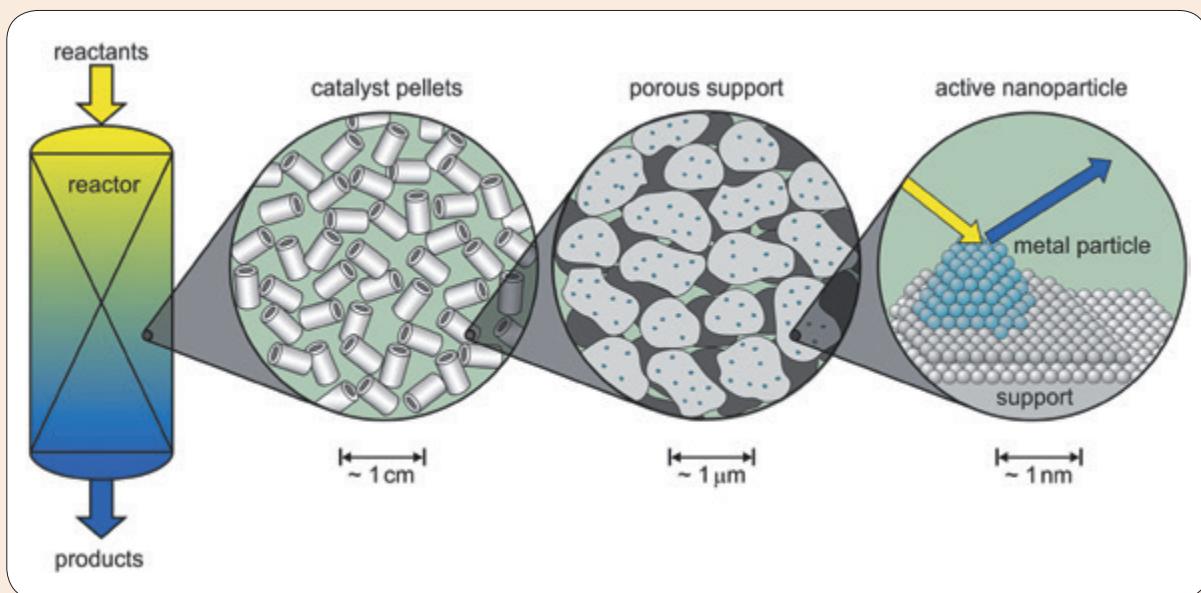
In catalytic reactors, microkinetics is overlapped by a variety of internal and external physical processes (Fig. 1) and this is also true for homogeneously catalyzed and electrocatalytic reactions. The resulting observable reaction rate can either be described by coupling the microkinetics with detailed physical models or by a macrokinetic formulation of the reaction rate, in which the observable rate is modeled by fitting empirical equations, such as power laws, to experimental data, so as to describe its temperature, concentration and pressure dependence.

Lectures on kinetics and elementary steps should include

- » Basics/definitions: Elementary reactions in catalysis as unifying concept, catalytic cycle, surface coverages, sticking coefficients, reaction rates and orders, types of mechanism (Langmuir-Hinshelwood, Eley-Rideal, Mars-van-Krevelen), complex reaction networks and their analyses (reaction flow, sensitivity, rate-determining steps, simplified rate equations such as Langmuir-Hinshelwood Hougen-Watson), kinetics and thermodynamics, microreversibility, adsorbate isotherms, types of surfaces/structures (crystalline phases, catalytic sites, washcoat, supports, chemisorption, textural properties), impact of adsorbate interactions and in-operando catalyst modifications on kinetics.
- » Modeling approaches to derive elementary steps, catalytic cycles and microkinetic rate questions: Density Functional Theory (DFT), Molecular Dynamics (MD), kinetic Monte Carlo (kMC), Mean-field approximation (MF), intrinsic rate equations.
- » Kinetics for different types of catalysis (homogeneous, heterogeneous, biocatalysis, electrocatalysis and others)
- » Limitations on the reaction rate by internal and external heat and mass transfer limitations (macrokinetics): pore diffusion, intraparticle heat transfer, external diffusion, flow field, mixing, conductive/convective/radiative heat transfer, heat/mass transfer at fluid and catalyst interfaces, Thiele modulus, Damköhler number, effectiveness factor.
- » Measurements and evaluation of kinetic data: surface science tools for microkinetics, conventional integral and differential flow lab reactors, novel lab reactors (capillary, laser, NMR, and X-ray techniques) for in-

operando resolution of spatial and temporal profiles of gas-phase, concentration, temperature, surface coverage and catalyst state.

- » Impact of kinetics on reactor design/operation: Relation with conversion, selectivity, yield, side-products, reactor typ/size/operational mode, operating conditions, safety concerns (exothermicity), heating/cooling, aging and fouling, maintenance.



**Fig. 1: Catalyst action at multiple length scales from the reactor down to the atomic structure demonstrated here as example (source: Jan-Dierk Grunwaldt, KIT).**

- The kinetics of catalytic reactions depends on species concentrations, temperature, surface coverages (where applicable), catalyst state, which all can change in operando.
- The observed macrokinetic reaction rate results from interactions between the microkinetic rate of the elementary reactions and heat and mass transport processes in the reactor.

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# 5 Testing of Catalysts

## 5.1 Testing of Catalyst Properties

The performance (activity, selectivity, stability) of a catalyst is critical for its use in any given value chain and for the in-depth understanding of its mode of operation. Therefore, the testing and performance evaluation of catalysts is vital to be treated within the scope of teaching and to explain the underlying principles. It should be addressed which parameters have to be assessed through catalyst testing and which measures can be derived from them. Also, the appropriate means and pitfalls of catalyst testing should be taught mentioning boundary conditions and general considerations. Besides the relation of testing to catalytic kinetics, elementary steps and mechanisms as well as the physical catalyst properties, the lectures should include the discussion of typical reactors and testing set-ups, including analytical techniques that are typically used in catalyst performance evaluation. The following topics should be referred to:

- (I) definition of generic performance parameters: conversion, selectivity, yield
- (II) catalyst lifetime, deactivation
- (III) general considerations for catalyst testing and interpretation of obtained data (isothermicity, mass transport limitations, differentiation of governing phenomena)
- (IV) reactors for catalyst testing (description of different reactor types and scales for catalyst testing, discussion of specifics of reactor types and suitability for challenges to be addressed), generation of reactor feeds, devices for product sampling and analytical techniques for product characterization.

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## 5.2 Approaches for Rapid Catalyst Performance Assessment: High Throughput Approaches

Under the umbrella “High Throughput Experimentation in Catalysis” an overview of the principles of high throughput experimentation and the application of such techniques in the context of applications in homogeneous, heterogeneous and biocatalysis applications should be taught.

It should be made clear that the term high throughput experimentation refers to execution of different experimental stages in a fast, integrated and reproducible fashion. Typical elements that can be recognized in the field are approaches of parallel mode of action or fast sequential execution of operations. Both parallel operation and fast sequential execution can be employed as guiding principles for the application fields of synthesis of catalysts for both homogenous and heterogeneous catalysis, the testing of catalysts as well as the analysis of materials used as catalysts.

The typical flow of work that should be discussed is the widely accepted “Design-Make-Test-Model” flow. This flow of work illustrates that high throughput experimentation is a well thought over effort which largely relies on well thought over experiments, planned on the basis of accepted mathematical tools and on feedback loops concerning catalyst performance and/or other catalyst properties; the flow of work stresses the vital aspect of

data handling and communication in between the different steps and the iterative cycles. In the context of this teaching content, different strategies for treatment of data and model strategies for model based data analysis and experimental design should be introduced and discussed.



**Fig. 2:** 16-fold high throughput reactor system for high pressure operation. The unit is designed to perform reactions relevant for refinery catalysis and fuels upgrading like hydrodesulfurization, hydrodenitrogenation or hydrodeoxygenation (source: hte GmbH).

Another vital aspect that needs to be touched in the context of the lectures are the specific demands that occur and can be covered in high throughput programs with technically differing focus and have a huge impact on the design of the program as such: the most important differentiation are programs with the goal of screening new catalyst candidates for prospective hits in difference to programs with the goal of optimization of one or a set of given catalyst candidates from a materials point of view and/or the optimization of a reaction corridor, i.e. temperature, partial pressures, relative velocity and others (Fig. 2). Other types of testing programs entailing optimization may include kinetic investigations or the investigation of ramp- or -down procedures.

The lectures should be rounded up by illustrative and didactically valuable application examples.

- Testing the performance of a catalyst is critical for the in-depth understanding of its mode of action.
- High throughput experimentation in catalysis allows fast and efficient evaluation of catalysts and reaction conditions with the purpose of optimization towards a given target.

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# 6 Characterization of Catalysts

## 6.1 Introduction

A knowledge-based design of catalysts and subsequent optimal reactor designs require a detailed characterization of catalyst structure including the assessment of kinetics. For molecular and enzymatic catalysts, mainly spectroscopy in the liquid phase including techniques like IR, Raman, NMR of different nuclei, EPR, EXAFS and UV-Vis is employed for their study; generally these techniques are capable of revealing a good understanding of all elementary steps in the respective catalytic cycles. For solid catalysts, various additional aspects on different levels have to be considered and should be taught accordingly:

- (I) Characterization of the microstructure and structural dynamics on a molecular level to gain understanding of the elementary processes at the active site, on the surface or at the interfaces, which is also relevant for homogeneous and biocatalysis (physical/chemical level).
- (II) Characterization on a macroscopic level to support design of solid catalysts, determination of global reaction kinetics as a basis for designing and operating the reactor (engineering level).

Atomic level understanding is often helpful to improve kinetics, gain insight into active sites, reaction intermediates, promoters and poisons, and to understand the evolution of the active catalyst and its deactivation on a microscopic level. As catalysts are usually very dynamic under reaction conditions approaches, spectroscopic studies under reaction conditions are especially important for elucidation of catalyst performance (activity, selectivity, stability). Such approaches are especially valuable, if augmented by coupled on-line product analysis (operando spectroscopy). This allows correlating catalyst microstructure and catalytic performance. Studies of this kind are often complicated by the coexistence of so called spectator species on the catalyst surface: the use of transient techniques is a valuable approach for the discrimination of these species and should be taught accordingly.

Equally important is the engineering side (see chapter 7 reaction engineering): for practical applications and meaningful testing of catalysts, fundamental properties like specific surface area, particle shape, porosity and mechanical stability play an important role. Global reaction kinetics is required for reactor design. Likewise, heat and mass transfer need to be characterized. Hence, a full multi-scale characterization for phenomena associated to the different length scales is required as indicated in Fig. 1. Also, the different time scales observable with the corresponding techniques should be dealt with.

The results obtained from characterization are the basis for reactor engineering and atomic scale analysis as outlined below. The challenges are demonstrated here for solid catalysts, whereby the emphasis is laid on the strategic approach, namely the use of the above mentioned toolbox of complementary methods that should be taught accordingly. Many of the tools available for solid catalysts are given in Fig. 3; their application will strongly depend on the problem under discussion.

## 6.2 Characterization of the Macroscopic Structure of Solid Catalysts

For characterization of formulated catalysts with respect to the surface area, shape, density, porosity, mechanical stability etc., a number of well-established techniques is available, e.g., electron and light microscopy, density measurements, standardized crushing and attrition tests, textural analysis by physisorption of gases such as N<sub>2</sub>, Ar or CO<sub>2</sub> as well as mercury porosimetry. Tomographic methods using X-rays or electrons are an emerging field allowing the visualization of shell impregnation, washcoat layer formation and pore connectivity on all length scales. In addition, X-ray or neutron based scattering techniques like SAXS or SANS are important.

The quantitative determination of catalytic reaction rates can be made using different reactors, the characteristics of which must be taken into account. Influence of heat and mass transfer can be detected by rate determination at

different linear gas velocities and with different sieve fractions (see also chapter 4 Kinetics and Elementary Steps and chapter 5 Testing of Catalysts).

### 6.3 Characterization of the Microscopic Structure of Solid Catalysts

For studies on the atomic scale, catalysts need to be analyzed by multiple techniques, since no single technique gives access to full information necessary to elucidate a catalyst microstructure. Nowadays a full toolbox of complementary methods is available (see Fig. 3). Although many of them are taught in physical chemistry or physics courses, a detailed discussion on the basic principles is necessary to understand their particular use and limitations in catalyst characterization. It is advised to connect the discussion of the methods with specific examples from technical application and the literature.

Treatment should cover physi/chemisorption, temperature-programmed methods (TDS, TPR, TPO, TPS) including thermoanalytical methods (TGA, puls-TGA, DSC). Structures can be determined by various scattering and spectroscopic methods using X-rays, electrons, or neutrons. Surface and bulk sensitivity (short penetration depth of electrons/ions compared to X-rays) for XPS, ISS, EELS, AES, TEM, SEM (surface) and XRD, SAXS, XES, EXAFS (bulk) as well as the particle-wave dualism play an important role in understanding the methods. Next, spectroscopies like

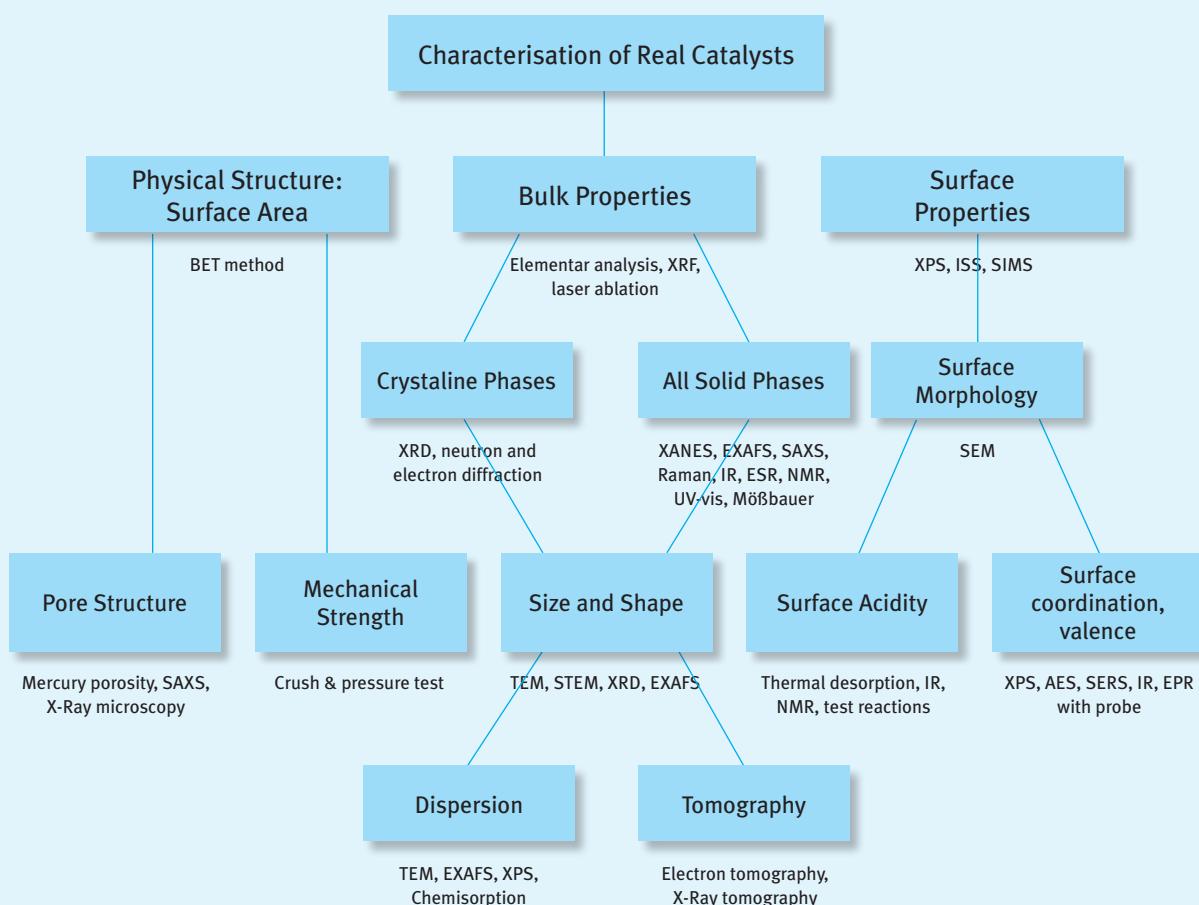


Fig. 3: Process-driven or “problem-solving” characterization approach for analyzing catalysts on multiple length scales (abbreviations are given in the appendix) (source: adapted from ref. [3]).

vibrational (IR, Raman), Mößbauer, NMR, EPR and UV-vis need special attention. Although it is often valuable to give an overview over the different techniques, it is most important that students understand which problems can be solved and where are limitations of the technique employed. (Fig 3). Last but not least the characterization of catalysts by their kinetics, selectivity and stability is very important (see also section 4) and can be combined in a beneficial way during operando characterization studies with structural probing.

#### 6.4 Deeper Understanding: Single Crystal Surfaces and In Situ/ Operando Studies

Catalysis research benefits a lot from surface science work with idealized catalyst models of different degrees of complexity (see Section 6.1) – although it must not be forgotten, that those techniques work far from industrial process conditions. Typical methods used in such work might be used to illustrate important principles (LEED – 2d diffraction, reciprocal space; scanning probe microscopies as alternative imaging techniques).

It is now generally accepted that characterization of a catalyst in its working state evidenced by simultaneous measurement of catalytic performance (operando studies) or under specific conditions of temperature and atmosphere (in situ studies) provide the best opportunity to discover active sites and intermediates because catalyst structure may change under reaction conditions. Operando studies combine simultaneous investigation into structure and catalytic performance on one sample, which is a demanding task and cannot be realized without compromises. For X-ray based techniques or spectroscopies at different wave lengths, the reactor needs transparent windows. Special designs are required for microwave- or radiofrequency-based techniques such as EPR and NMR. Synchrotron-based methods which can exploit the high source intensities should receive special attention, also towards spatially resolved and microscopic studies. Recently also electron-based methods have moved in this direction, allowing for in-situ studies in the mbar, recently even in the bar range.

Treatment of this topic should include strategies of cell design for work in stationary and transient regimes (as a trade-off between engineering and spectroscopic requirements), cell design for spatially resolved investigations, e.g., to elucidate catalyst states along a reactor, opportunities and limitations of coupling several operando methods in a single experiment and case studies including gas-phase and liquid phase, but also high-pressure and other demanding reaction conditions.

- Characterization of the micro- and macrostructure to cope for fundamental and engineering aspects.
- Use of complementary methods of the toolbox.

## 6.5 Appendix

AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
BET	Brunauer-Emmett-Teller adsorption isotherm
DSC	Differential Scanning Calorimetry
EELS	Electron Energy Loss Spectroscopy
EPR	Electron Paramagnetic Resonance
ESR	Electron Spin Resonance (= EPR – electron paramagnetic resonance)
EXAFS	Extended X-ray Absorption Fine Structure
IR	Infrared Spectroscopy
ISS	Ion Scattering Spectroscopy
LEIS	Low Energy Ion Scattering (other name for ISS)
LEED	Low Energy Electron Diffraction
NMR	Nuclear Magnetic Resonance
SAXS	Small Angle X-ray Scattering
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
STEM	Scanning Transmission Electron Microscopy
STM	Scanning Tunneling Microscopy
TEM	Transmission Electron Microscopy
TDS	Thermal Desorption Spectroscopy (typically under vacuum, surface-science-technique)
TGA	Thermogravimetric Analysis
TPO	Temperature Programmed Oxidation
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
TPS	Temperature Programmed Sulfiding
UV-vis	Ultraviolet Visible Spectroscopy
XANES	X-ray Absorption Near Edge Spectroscopy
XAS	X-ray Absorption Spectroscopy
XES	X-ray Emission Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

### References

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# 7 Computational Catalysis

Computational catalysis is a toolbox which can be applied for all types of catalysis or catalyzed reactions. Computational catalysis utilizes approaches of statistical mechanics, kinetics, classical and quantum mechanical calculations to investigate elementary reaction steps, entire reaction mechanisms, their thermodynamics and microkinetics [1-3]. Additionally, multi-scaling procedures are used to integrate this description into simulations at model catalyst pellet and chemical reactor level (see Chapter 6 Characterization of Catalysts). Initially, a concept of the possible elementary reaction steps has to be developed. This still rests largely on chemical knowledge and intuition. Reaction network generators and path-finding algorithms may also be used. The same holds for the active centers which are in general not known at the outset. Inclusion of spectroscopic data is often useful.

Next, enthalpies of adsorption and barriers of all reaction steps have to be calculated. This is a genuine quantum mechanical task, at present largely done at density functional theory level [4]. More accurate wave-function based approaches are used for benchmarking, or for molecular catalysts [5, 6], while scaling-relations are used for computational screening studies [3]. Rate constants from this data are generally obtained through transition-state theory. The microkinetic modeling is either done at mean-field level or through dedicated kinetic Monte Carlo (kMC) simulations [6]. The appropriate consideration of lateral interactions at this level is still developing. If all the necessary thermodynamic and kinetic data are calculated the full micro-kinetic reaction scheme can be run for example by mean-field codes like CHEMKIN or CatMAP, or kMC codes like kmos or zacros. If diffusion and adsorption inside the pellet have to be included, multicomponent adsorption and diffusion have to be calculated by Monte Carlo (MC) and Molecular-Dynamics (MD) simulations in the proper ensemble [8]. At present, such simulations are almost exclusively done at force-field level. Force-field development is a time consuming task of its own. Finally, a full reactor simulation can be executed using a plug-flow or dispersion model, whereby all the above mentioned data are used [10-11]. These tasks imply that the student has to learn the fundamentals of Quantum Mechanics, Statistical Thermodynamics, classical and quantum modelling as well as corresponding computer-based methods.

- Computational catalysis gives fundamental insight into the details of catalytic reaction mechanisms.
- Computational catalysis utilizes statistical thermo-dynamics, quantum mechanics and molecular simulations as tools.

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### General Introductions

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### Quantum Chemistry

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# 8 Reaction and Process Engineering

## 8.1 Introduction

For the development of new industrial processes or for improving existing industrial processes catalysis is one of the key technologies. It is important for the student to understand that reaction and process engineering are both technical means which via alternative reactor designs, (e.g., microreactors), and/or process design, (e.g., process intensification) lead to the final technical process for any type of catalysis or catalyzed reaction, independent of the type of catalysis (e.g., homogeneous, heterogeneous, biocatalysis or the like). Altogether economic viability and legal regulations are the main impulses which define the target corridor into which the process has to be tailored in. The key technologies of reactor and process design are used to achieve at a given energy expense for all unit operations a given corridor of conversion, selectivity and finally space time yield to target products, including desired product specifications that have to be met. It is of utmost importance to introduce the concept of scale-up and –down via introduction of scalable key technologies. For the case of new processes, scalability usually comprises an up-scaling from the lab to the production scale or in the case of existing processes a down-scaling to laboratory scale that has to be done. It is considered useful to teach this topic following practical examples: The so-called microactivity test (MAT) is a test unit which mimics catalyst behavior in a riser reactor for fluid catalytic cracking, by injecting a certain oil amount on the top of the fixed bed reactor where it evaporates rapidly and expands through the catalyst bed within seconds (Downscaling). The MAT-technology is today developed to such a high level of sophistication that it allows precise prediction of catalyst and plant behavior and is used by the industry for the development of complex cracking catalyst formulations. The hydrogen peroxide to propylene oxide (HPO) process developed by BASF/Solvay and Evonik/Uhde is an example of a successful up-scaling from the lab into production scale via defined unit-operations and the so called “mini-plant technology”, namely small scale units which allow closure of recycle loops.

## 8.2 Heat and Mass Transport Phenomena

One of the crucial phenomena when changing the scale between lab and industry, and vice versa, is the relevance and impact of heat and mass transport phenomena. These effects are especially pronounced for catalysts used at laboratory scale, with particle sizes of less than 1 mm and shaped catalysts used in a fixed bed reactor which can be of the size of 5 mm and more. Heat and mass transport limitations can occur which change the utilization factor of the catalyst and therefore performance characteristics drastically. Therefore, the understanding of the underlying phenomena and how factors of mass and heat transport limitations can be evaluated and measures can be taken should be taught. Similar considerations come into play for the reactor technologies, especially with regard to heat management. In the laboratory often only some milliwatts have to be removed by heat loss towards the environment without active cooling. This means that laboratory operations can be conducted isothermally without taking great care to design features of reactor systems. In production scale kilowatts or megawatts of heat is generated and needs to be removed by actively cooling and thoroughly designing the reactor.

## 8.3 Tailored Reactor and Process Concepts

With regard to the reactor design the degree and time-spans of mixing of reactants plays a significant role, which means that fluid-dynamics can strongly affect catalyst performance (activity, selectivity and stability). Reaction and process engineering issues need to be considered when lab-scale catalyst testing should allow scalability of the results between lab and production scale. The so-called ideal or idealized reactors are important laboratory tools in experimental reaction engineering to guarantee defined fluid-dynamics; two extremes are typically used for experimentation, depending on the questions to be answered by the experiment. So-called fully back-mixed reactor systems like continuous stirred tank reactors on the one hand and the non back-mixed systems like the ideal plug-flow reactors on the other hand are key technologies which find widespread application. These reactor systems allow the precise determination of the kinetics of the reaction system at laboratory scale. Provided that also any situation of heat and mass transport limitation can be avoided an intrinsic kinetics, called micro kinet-

ics, can be determined. On the basis of such micro-kinetic data-sets of a given catalyst system, every degree of backmixing and/or of heat and mass transport limitation can be estimated on a scale relevant for an industrial reactor theoretically or by simulation.

## 8.4 Aspects of Industrial Catalysis

From the industry's point of view, most critical parameters of a catalyst are activity, selectivity, lifetime, costs and the ability of integration into an economic process scenario. Any catalyst inside the reactor has to withstand mechanical and thermal stress. For solid catalysts particle design and loading patterns have to be optimized in a way to minimize pressure drop and maximize accessible geometric surface area at the same time. In cases of deactivation caused by coking or poisoning, viable regeneration scenarios must be developed that allow commercially attractive operation. If expensive noble metals are used as active components, these must be recovered to a maximum percentage by recycling of the spent catalysts. Compared with the value of the products (selling price) obtained in catalytic processes the costs of catalyst are quite moderate, e.g., approximately 0.1% in petroleum refining or 0.2% in petrochemical processes. However, as the turnover (number of converted molecules per active site) may reach values of  $20 \cdot 100 \cdot 10^6$  before requiring regeneration, recycling or disposal, the added value (benefit created per cost of catalyst and lifetime) can reach average numbers of 100. Therefore it is hardly surprising that the global market for catalysts and catalyst regeneration reached nearly \$23.2 billion and nearly \$24.6 billion in 2013 and 2014, respectively. This market is forecast to grow at a compound annual growth rate (CAGR) of 4.0% to reach \$29.9 billion in 2019 [1]. This growth can only be realized, if catalysts with even better

performance are commercialized. However, the development of new or improved industrial catalysts can be an expensive and time consuming operation, depending on the chemical reaction to be catalyzed, on the knowledge and equipment already available and on the proposed scale of the process. The three main motivations result from a change in marketing or raw materials conditions, from a change in government legislation or from the desire to optimize the performance of the plant already in existence [2].



Fig. 4: Citral plant at BASF Ludwigshafen site as an example for applied reaction and process engineering. Citral is a key chemical intermediate to produce fine chemicals like vitamins, fragrances or aroma-chemicals (source: BASF SE).

production processes are important courses to understand the reaction and process engineering issues. It is suggested to include illustrative examples from industrial realization in this section (Fig 4), additionally the Lehrprofil Technische Chemie [3] nicely summarizes the recommended course contents. It is especially important to mention in the context of the examples that different types of catalysis require different types of reaction and process engineering.

- Catalysis engineering relies on an integrated design on the reactor and the process level.
- Up- and downscaling as well as heat and mass transfer are important key issues to be considered for catalytic processes.

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# 9 Types/Classes of Catalysts

## 9.1 Catalysis on Surfaces

### 9.1.1 Principles and Definitions

In heterogeneous catalysis the catalyst materials are solids, which are applied in gas, liquid or gas/liquid phase reactions and the reaction takes place at the solid catalyst surface. Specific interactions of the adsorbed reactants with the surface lead to certain reaction pathways which can be described by elementary steps that involve lower activation energies as compared to the uncatalyzed reaction. If several catalyzed reactions are possible, the difference in the respective activation barrier determines the selectivity of the catalyst for the desired reaction. Certain structural features, e.g., defects or reconstructions, and the specific chemical composition of the surface under reaction conditions are important for the catalyst performance. Characteristic descriptors useful for industrial catalysts are activity (including stability), selectivity and factors, such as mechanical and chemical stability (against attrition and other phenomena causing loss of mechanical stability), shape (resulting in pressure drop in a given reactor) and regenerability. It is important to introduce these basic concepts of heterogeneous catalysis to the students to create a basis which can be built on.

### 9.1.2 Mechanisms

Basic concepts of kinetics and underlying phenomena and resulting mechanisms (Physi- and Chemisorption, Freundlich, Langmuir and Brunauer, Emmett and Teller, Langmuir-Hinshelwood, Eley-Rideal,) should be addressed. Regarding the theoretical aspects of active surface sites the historic development should be taken into account and illustrated (e.g., Taylor or the Hedvall effect). In order to teach the theory of active sites the following three topics are essential: Geometric/sterical influence of surface atoms (e.g., Boudart principles), Energetic influence of reactant-surface interactions (e.g., Sabatier principle) and the influence of electronic factors (d-band model, ligand effects, ensemble/cluster effects).

### 9.1.3 Classification

Generally, bulk catalysts, supported catalysts, and coated catalysts can be distinguished as separate catalyst classes and should be introduced as such. The class of bulk catalysts comprises metal gauzes, metal foams (Raney-type metals), fused composites as well as crystalline and amorphous oxides and sulphides. Supported catalysts contain a highly dispersed active phase spread at the surface of a support material. Often oxides with high or at least tunable specific surface area are used as support material. The active components include highly dispersed metals, oxides/sulphides/nitrides/carbides as well as supported liquid phases. Deposition of washcoats (oxides and PGM) on monolithic supports, e.g., ceramic materials, with unidirectional macro channels are examples of a coated catalysts used in very often in environmental catalysis like automotive emission control catalysis.



Fig. 5: Examples of solid catalysts in the form of shaped catalyst bodies as applied on an industrial scale (source: BASF SE).

#### 9.1.4

#### Preparation of Solid Catalysts

The entire spectrum of tools in synthetic inorganic chemistry, including high temperature methods, precipitation, solvothermal synthesis, sol-gel chemistry, chemical vapor deposition (CVD), and soft matter techniques adopted in part from organometallic chemistry, have been applied to synthesize supports, supported catalysts and bulk catalysts. The synthesis of supported thin layers or highly dispersed metals or oxides is performed for example by wet or dry impregnation including specific ion exchange methods, deposition precipitation, electrochemical deposition, anchoring and grafting via liquid phase techniques, or atomic layer deposition (ALD). In addition to process-adopted design of the active phase itself, various shaping technologies have especially a great importance for the preparation of catalysts on an industrial scale; such methods are amongst others pelletizing, granulation, extrusion, or spray-drying. Parameters such as mechanical stability, thermal conductivity, pressure drop, and mass transport need to be taken into consideration. Special care has to be taken to introduce methods which are common in industrial catalyst production and to discuss the issue of scalability of synthetic operations (see Fig. 5).

#### 9.1.5

#### Characterization of Solid Catalysts

A broad spectrum of techniques is available today that render the investigation of freshly synthesized catalyst precursors, spent catalysts and catalysts under real working conditions (see Chapter 4 Kinetics and Elementary Steps): electron microscopy, BET method, XPS, X-ray (neutron) diffraction/scattering, X-ray absorption, NMR, EPR, vibrational and UV-vis spectroscopy, Temperature-programmed methods, thermal analysis, calorimetry, and chemical analysis. It is advised to introduce these techniques together with adequate and illustrative examples which illustrate their respective field of application and the value of the information obtained.

#### 9.1.6

#### Examples from Industrial Application

Processes involving heterogeneous catalysis are the technology basis for a wide spectrum of different industries (e.g., chemical and petrochemical industry). But also the state-of-the art manufacturing of cars would not possible without exhaust cleaning technologies applying heterogeneous catalysts beneficially. A summary of selected heterogeneous catalysis examples (ammonia synthesis for principles and mechanism and the other examples for typical classes and preparations of catalysts) is presented in Table 1.

**Table 1: Examples of important catalyst types and products from heterogeneously catalyzed processes.**

Classification of Catalyst	Reaction	Application
Bulk or supported catalyst	Hydrogenation	Ammonia
Bulk catalyst (Oxide)	Oxidation	Acrylic acid
Porous bulk catalyst (Zeolite)	Cracking	Gasoline and olefins
Supported catalyst (Metal)	Hydrogenation	Ethylene (ethyne)
Coated catalyst	Oxidation and SCR	Auto emission control
Supported single site catalysts	Polymerization of olefins	Polymer production

- Heterogeneous catalysis is an important means for chemical transformations in the chemical and petrochemical industry.

#### References

##### Literature Recommendation:

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## 9.2 Molecular Catalysis

### 9.2.1 Principles and Definitions

A homogeneously catalyzed reaction is characterized by all reaction components to be in a single liquid phase whereby the catalyst is a molecular defined structure. The advantage of molecular catalysis is the ability to steer chemo-, regio- and stereo-selectivity by molecular design of the catalyst which can in many cases not be achieved with multisite heterogeneous catalysts. A challenge, mostly encountered as relevant in technical applications, can be the required separation of the catalyst from the homogeneous reaction solution. This separation can be achieved by a two phase system where the catalysis takes place in one phase and the products migrate to the second phase and are thus separated ("multiphase catalysis"). The coating of a hetero-geneous support with a homo-geneous catalyst or the coating of a support with a liquid carrying the catalyst are two further elegant ways to separate the reaction products efficiently from a molecular catalyst.

Molecular catalysis should be taught by using the guiding principles mentioned in the following subchapters and the basic principles of the initial chapters. These guiding principles help the student to understand the essence of the nature of molecular catalysis and build a bridge towards the technical application.

### 9.2.2 Mechanisms

Not only is the catalyst itself a defined molecule, the mechanism of the catalysis is characterized by a number of also observable molecular structures that transform into each other to form a catalytic cycle consisting of elementary steps like oxidative couplings, migratory insertions or reductive eliminations. In understanding the mechanisms relevant in molecular catalysis, a basis for the student is created which has platform-like character. An example, the hydrogenation of a 1-alkene with hydrogen to an alkane using the Wilkinson complex  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  is shown in Fig. 6.

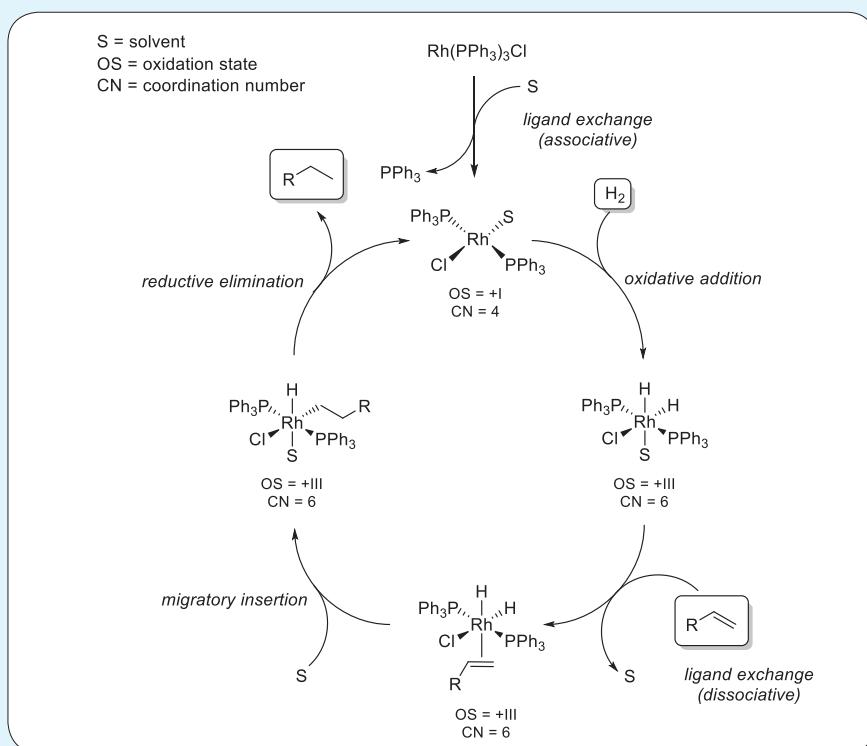


Fig. 6: Catalytic cycle of alkene hydrogenation with the Wilkinson complex  
 (source: Walter Leitner, RWTH Aachen).

### 9.2.3

#### Classification

Molecular catalysts can be divided into different classes: The catalyst can be

- » a soluble acid or base,
- » an organic compound (“organocatalysis”),
- » a soluble or immobilized enzyme (see chapter 9.3),
- » or a transition metal salt or complex.

The classification of molecular catalysts is vital as this systematic tool allows better overview over the whole field. It is important to remark that transition metal catalysis is especially versatile, because both the metal and the different complex ligands can be varied in manifold manner. Comparing heterogeneous and homogeneous catalysis homogeneous catalysts have certain specific features:

- » Their structure is well defined and can easily be “tailored” via ligand exchange thus varying electronic and steric properties of the catalyst. This often makes them highly selective.
- » Because of their solubility in liquid reactants or solvents they can be analyzed *in situ* by various spectroscopic methods.
- » Due to their complete solubility on a molecular level they are highly active already at very mild reaction conditions.

The molecular catalysts can also be classified via the reaction type they catalyze. Transition metal catalysts are very useful both in the synthesis of bulk and fine chemicals because they catalyze a great number of different reaction classes. Only some important examples are listed in the following:

- » C-C-linkage reactions, like oligomerizations, polymerizations, telomerizations,
- » hydroformylations, carbonylations and coupling reactions with aromatics
- » Metathetic redistributions of alkylidene groups of alkenes
- » Hydrogenations, especially enantioselective hydrogenations with hydrogen or transfer hydrogenations
- » Oxidations forming aldehydes, ketones, epoxides or carboxylic acids
- » Aminations, e.g., of halides, alkenes, dienes or alkynes
- » Isomerization of C-C-double bonds or skeleton rearrangements

### 9.2.4

#### Preparation

The preparation of the catalytic complexes is very well known from organometallic chemistry. It is suggested to include a limited number of characteristic examples within the curriculum. Thus every molecular catalyst is clearly defined by its stoichiometry and structure. The synthesis of the catalyst can be reproduced and the properties of the catalyst can be checked by several physicochemical and chemical methods. The active catalyst species can be synthesized in advance or “*in situ*” which means that the catalyst is formed in the reaction vessel starting from a metal precursor and the ligand. Obviously the latter method is very favored in industrial applications.

### 9.2.5

#### Characterization

A valuable feature of homogeneous catalysis is the ability to directly observe the catalytic species as well as surrounding reaction solution. UV/visible spectroscopy, IR spectroscopy can visualize both the content of the reaction solution as well as the catalyst. NMR spectroscopy of different nuclei (proton, phosphorus and the transition

metals used in the catalyst) are just as helpful as mass spectroscopy to characterize the catalyst itself. To determine the potential loss of transition metals during the catalysis the inductively coupled plasma – optical emission spectroscopy (ICP-OES) is of high importance. Lectures should touch on the topic of characterization and allow insights into methods and applications through illustrative examples.

### 9.2.6 Examples

The following list of homogeneously catalyzed industrial processes gives an impression of the impact of molecular catalysis on the industrial level. It is suggested to align contents of the application examples with the lecture content of the previous sections:

- » The selective Rh-catalyzed hydroformylation of propene to n-butanal, an important starting compound to polymer plasticizers
- » The oligomerization of ethylene to 1-alkenes in the so-called “Shell Higher Olefin Process (SHOP). These 1-alkenes are useful starting compounds for a number of nonionic or anionic detergents.
- » The double hydrocyanation of 1,3-butadiene to adipodinitrile, the precursor of a number of polyamides
- » The enantioselective hydrogenation of an imine to the herbicide metolachlor (Fig.7).

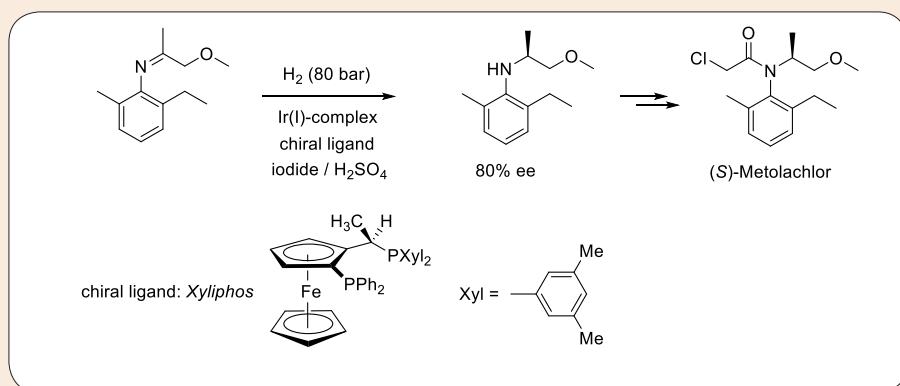


Fig. 7: The enantioselective step in the route to the herbicide metolachlor  
(source: Walter Leitner, RWTH Aachen).

- Molecular catalysts are of high importance in the synthesis of both bulk- and fine chemicals.
- The versatile tailoring of the catalysts enables high chemo-, regio- and enantioselectivities.

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## 9.3 Biocatalysis

### 9.3.1 Principles and Definitions

Biocatalysis is the acceleration of chemical reactions by biocatalysts: free enzymes or microbial cells. Biocatalysts are distinguished from molecular and solid catalysts by the fact that the catalytically active site is embedded in a protein backbone. There is a distinction between single enzymes (free enzymes), which are used as free or immobilized biocatalysts and living cells, where one or a consortium of enzymes are active in a cellular chassis (whole-cell biocatalysts). The biocatalysts in the latter two examples are present in a separate phase than the reactants and, thus, cases of heterogeneous biocatalysis from the viewpoint of reaction control.

### 9.3.2 Mechanisms

Teaching should address the history of biocatalysis, bioanalytics, enzyme nomenclature in respect to enzyme function and cofactor requirement, basics of protein biochemistry, enzyme kinetics (e.g., Michaelis-Menten, fundamental mechanistic types), microbiology, growth kinetics (Monod), bioreaction engineering (stoichiometry, mass balances, mass transfer, energy transfer, yield concepts, impact of thermodynamics, quantitative description of batch and continuous processes).

Typical mechanistic features are characterized by enzymes as biocatalysts containing or not containing cofactors, coenzymes, multiple active sites, and for whole cell biocatalysts in addition by energy regeneration/transformation or the ability of self-regeneration. The turnover number of biocatalysts is determined by mass and energy transfer, enzyme and/or cellular kinetics and the total turnover number is determined by its stability.

### 9.3.3 Classification

Depending on the type of reaction control and – engineering, biocatalysts can be homogeneously or heterogeneously applied in reaction media. Mechanistically, biocatalysts are grouped in a distinct class next to chemical catalysts (homogeneously or heterogeneously controlled in reactions and processes).

- I) Classification via types of chemical reactions: Free enzymes are classified following the enzyme nomenclature published by the International Union of Biochemistry and Molecular Biology (IUBMB) into six enzyme classes. Sorting criteria are fundamental chemical reactions being catalyzed. Cellular biocatalysts (comprising regeneration of cofactor and enzyme, multistep reactions, compartmentalization).
- II) Classification of reaction sequences in respect to fundamental concepts in coupling individual biocatalyzed reaction steps (serial, tandem, domino, parallel, convergent)
- III) Catalyst classification via reaction engineering in respect to application mode

Biocatalysts are basically classified as free enzymes or whole-cell biocatalysts, used homogeneously or heterogeneously (immobilized, see above).

Teaching should address reaction kinetics, enzyme immobilization, cell immobilization, enzyme classes, enzyme technology, analytical methodology for quantifying and understanding the function of enzymes and of whole-cell biocatalysts.

### 9.3.4 Preparation

Biocatalysts are basically encoded on DNA by genes and functionality is often delivered via cofactors and coenzymes. Gene expression yields enzymes which are used either in cellular compartments or isolated as free enzymes. Teaching on biocatalysis should thus address issues of screening, selection and preparation of enzymes

and microorganisms likewise. For preparation of biocatalysts, methodology of protein biochemistry, microbiology, basic microbial taxonomy, and molecular techniques including enzyme engineering, metabolic and genetic engineering (including safety standards, "Gentechnikgesetz") should be covered.

### 9.3.5 Characterization Through Performance Data

The efficiency of biocatalysts is quantified by turnover number ( $k_{cat}$ ) and total turnover number. Teaching on biocatalyst characterization should cover reaction engineering, including kinetics, deactivation and activation, microbial cultivation and safety aspects for biochemical reagents. Most importantly, characterization must include reaction and process formats suitable for organic synthesis on a preparative scale. This also comprises biocatalyst-related integrated process design, product recovery and downstream processing and a quantitative evaluation of reaction and process efficiency (Fig. 8). Awareness for mass transport limitations in multiphase systems modulating biocatalyst performance should be imparted. In addition, bioinformatics (identification, design and data on biocatalysts), handling of databases, and analytics for small molecules, proteins, cells should be treated.

### 9.3.6 Examples

Application examples of biocatalysts (isolated enzymes and whole cells) can be found in numerous review articles and text books (see references below). Teaching should comprise selected reactions and processes in industry (company, typical market segments for products, reaction, process, product, productivity, product recovery, economics, green chemistry concepts) and forefront outstanding examples from academia (highlighting advantages and disadvantages), and catalysis-related issues of downstream processing (product recovery, separation techniques, purification, formulation). Special emphasis should be put on reaction media (aqueous, non aqueous, gas, liquid, solid) and process integration.

- Biocatalysis is the application of nature's catalysts (cells or enzymes) for chemical synthesis.
- Biocatalysts often show high regio-, chemo- and enantioselectivity for the conversion of natural as well as non-natural compounds, mostly in aqueous, but also in organic reaction media or even neat conditions at temperatures mostly between 20 and 40°C.



**Fig. 8:** A technician preparing a fermentation reactor for operation; keeping the conditions of the fermentation process adequate for optimum productivity of the respective microorganism is key to obtaining optimum performance (source: BASF SE).

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## 9.4 Photo-, Electro- and Multicatalysis

### 9.4.1 Introduction

Photocatalysis, Electrocatalysis and the combination of both, Photoelectrocatalysis, are catalytic processes of fundamental importance. Combining features of heterogeneous or homogeneous catalysis with additional electric parameters and variables, such as current, potential and resistance, they constitute the most complex catalytic interfacial charge transfer processes. Their key idiosyncrasy are „free“ charge carriers (electrons and holes), the generation, migration, and participation of which in the interfacial charge transfer are intrinsically coupled to the concomitant catalytic conversion (making/breaking) of chemical bonds. The catalytic conversions occur at and across electrified interfaces and electric fields in which „free“ charge-carrier tunnel to/from more localized electronic states (chemical bonds).

Photoelectrocatalysis has attracted tremendous attention as a key science and technology area to address the Grand Challenge of chemical energy storage and conversion necessary for the realization and integration of renewable solar energy systems. Motivated along these lines of arguments in the class room, students realize the broad appeal and importance of photo- and electrocatalysis.

Multicatalysis concepts, such as Synergistic or Dual Catalysis, involve two or more catalysts that act on distinct specific reactants/substrates simultaneously, enabling otherwise inaccessible reactions among the reactants.

### 9.4.2 Photocatalysis

In lectures about Photocatalysis it is very important to address the similarities, but also the differences to classical thermal catalysis. Major topics in teaching courses should include:

- » What is Photocatalysis: Heterogeneous vs. homogeneous Photocatalysis, Photocatalysis vs. thermal catalysis
- » Important reactions: Wastewater treatment, CO<sub>2</sub> reduction, water splitting, synthesis of chemicals via Photocatalysis, self-cleaning
- » Photocatalytic reactors and photoelectrochemical cells, light sources, light spectra and filters
- » Band gap determination, actinometry, quantum yields and photonic efficiency, photocurrent spectroscopy, Mott-Schottky analysis
- » Materials design, band gap engineering, absorbers and co-catalysts, abundance of elements

### 9.4.3 Electrocatalysis

Electrocatalysis is the key driver for electrochemical energy systems, such as fuel cells, electrolyzers as well as for electrochemical generation of chemicals and metals. The concept of electrocatalysis introduces the study of adsorption properties of the electrode surface combined with the study of the kinetics and mechanism of the elemental steps during the electrochemical processes at the electrode/electrolyte interface. The mechanism and rate of electrochemical reactions and their changes can be tuned by the structure or composition of electrode surface or reaction conditions.

Lectures about electrocatalysis should introduce:

- » Electrode kinetics incl. setups: elementary kinetics at ideal electrode surfaces, microkinetics at flat surfaces, e.g., rotating disk electrode, including Butler-Volmer and Nernst equation, macrokinetics at porous electrodes and electrode assemblies including mass-transport effects and kinetic losses for technical application (Fig. 9).
- » Electrode materials: Single crystal model systems, polycrystalline electrodes, nano-structured electrodes, precious, costly PGMs, concepts for reducing PGM loading such as nanoparticles on high surface area, conductive support and alloys or core-shell nanoparticles, abundant, PGM-free materials, electrochemically active enzymes/bacteria.

- » Analysis methods: dynamic electrochemical methods such as EIS, CV, chronoamperometry; intermediate/product analysis such as FT-IR, DEMS, XAS, SAXS, AFM, STM, XPS and TEM-EDX/EELS; scanning electrochemical methods such as SFCs and SECM; computational methods from thermodynamics/elementary kinetics (DFT, KMC) to micro- and macrokinetics (mass/charge balances), including multi-scale modeling
- » Important electrochemical reaction processes: H<sub>2</sub> oxidation/evolution; O<sub>2</sub> reduction/evolution; Cl<sub>2</sub> evolution, limitations on reactants/products (C-C-bond-breaking; poisoning; degradation)

#### 9.4.4 Synergistic/Dual/Multi Catalysis

Catalytic pathways often rely on the interaction of one catalyst with a single substrate, thereby lowering the energetic barrier to bond formation with a second, unactivated substrate. While this mono-catalysis strategy has successfully delivered vast numbers of new reactions over many decades, multi-catalysis concepts have recently begun to emerge that allow access to many difficult or unattainable transformations. In a stricter sense, multi or synergistic catalysis is defined as a process, wherein two or more catalysts and two or more catalytic cycles work in concert to create a single new bond. The term „multi or synergistic catalysis“ appears often in the context of homogeneous catalysis, less so in heterogeneous catalysis, where the concomitant activation of two or more reactants on the surface of a single catalyst is usually referred to as „bifunctional catalysis“.

- Photo- and Electrocatalysis are catalytic disciplines addressing the homo- or heterogeneously catalyzed electron transfer across an electrified interface for the purpose of bond making/breaking.
- Photo- and Electrocatalysis play key roles in the Science and Technology of electrochemical energy storage and conversion for efficient interconversion between electricity and chemical bonds. As such, they are instrumental for the integration of renewable electricity.

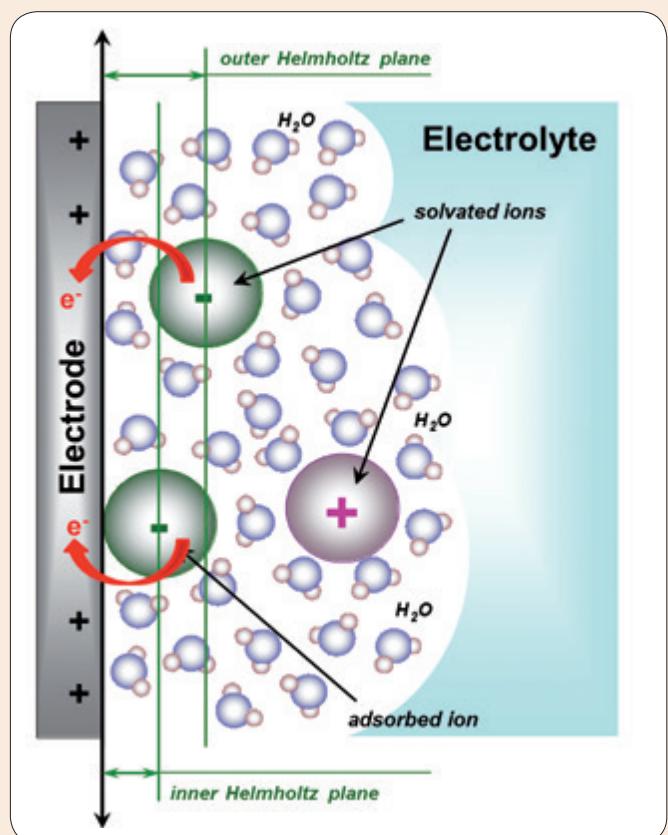


Fig. 9: Electrocatalysis promotes electron transfer between adsorbed or solvated reactants and an electronically conductive electrode across an electrified solid-liquid interface (Helmholtz plane)  
(source: Peter Strasser, TU Berlin).

Lectures about electrocatalysis should introduce:

- » basic concepts of multi catalysis illustrated by specific examples such as Carbonyl  $\alpha$ -functionalization, reactions of  $\alpha,\beta$ -unsaturated carbonyls, Carbonyl and imine 1,2-addition, Lewis base-catalyzed cycloadditions and cyclizations and related reactions.
- » It should be highlighted that this strategy may lead to several benefits, specifically synergistic catalysis can (I) introduce new, previously unattainable chemical transformations, (II) improve the efficiency of existing transformations, and (III) create or improve catalytic enantioselectivity where stereocontrol was previously absent or challenging.

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## 10 What's Next?

Under the umbrella “what’s next” a summary of topics in which new principles exploited for the purpose of catalysis and new general trends in catalysis applications should be treated. It seems useful to cover the topic of “what’s next” to an audience that has already been taught the relevant basis of catalysis and its applications. As the topic of “what’s next” is subject to (frequent) changes reflected by new directions and developments, the recommendations of how the topic should be taught can only be very general. The content covered here should also be strongly dependent on the personal assessment and the own research topics of the scientist teaching it, since for students it is important to get a glimpse of the current frontiers of catalysis research and technology by the colleagues defining them. It is suggested to split the topic structurally into the two subcategories mentioned above:

- I) **New principles in catalysis:** here new principles in catalysis of fundamental character should be treated. These principles should be discussed in the context of the fundamentals taught in section 2, to give the audience a contextual background. Examples that are suitable for explaining new principles in catalysis are “multi-catalysis”, where for instance catalytic cascade reactions are used for the synthesis of complex synthons [1]. Cascade reactions as such have been known, yet the coupling of cascades using differing types of catalysis in a single flask either in tandem or sequentially is new and the principle is applied in a variety of fields. Other examples for new principles exploited in catalysis are [2]:
  - » Expansion of photo- and electrocatalytic concepts,
  - » Dynamic operation modes,
  - » Tailor-made solvents for enhancing the reactivity/selectivity of catalytic reactions
  - » New materials with unforeseen catalytic modes of action for new and known catalytic applications,
  - » Synthetic catalytic “machines” analogous, for instance, to ribosomes, on surfaces or as molecular units.
  - » Retrosynthetic planning of combination of chemo- and biocatalysts [3]
  
- II) **New general trends in catalysis applications:** here new trends where catalysis is applied should be summarized. Typically such fields of application will make use of certain areas and aspects of catalysis as a tool to reach a certain target which will in many cases be economically motivated, other motivations may involve aspects of sustainability or the like. As these trends can make use of differing aspects of catalysis it is strongly suggested to discuss this topic with an audience that has already received the information of the previous chapters. A prototypic example is the use of catalysis for converting renewables into products of value. This trend in catalysis is motivated by aspects of sustainability, but has strong economic ties. Also for this part “new general trends in catalysis applications”, it is suggested to link the discussion to related topics discussed in the previous sections, illustrating the fundamental principles that are being applied. Other examples of new trends are [2]:
  - » **Resources:** more robust catalysts for processing of impure raw materials; platform chemicals based on renewables; value chains based on carbohydrates (instead of hydrocarbons); direct conversion of methane and CO<sub>2</sub>
  - » **Energy:** expansion of catalytic processes based on renewable energy sources; more efficient catalysts for hydrogen evolution; improved electrocatalyst and electrode development
  - » **Environment:** more stable and efficient catalysts for industrial/automotive exhaust gas purification and waste water treatment; direct and atom-efficient synthesis routes for the production of fine chemicals

- » **Reaction engineering:** development of multifunctional catalytically active membranes combining chemical reaction and product separation; Additive manufacturing for novel types of catalytic reactors, components for catalytic reactors, and possibly even structured supports
- » **Modelling in the field of Catalysis in the light of “Industry 4.0”:** Improved multiscale modelling of catalytic materials for dedicated applications.

The future of catalysis will be influenced by

- new catalytic principles and
- innovative catalytic applications.

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## IMPRINT

### Authors

Marc Armbrüster	TU Chemnitz (Chapter 3)
Marcus Bäumer	Universität Bremen (Chapter 9.1)
Arno Behr	TU Dortmund (Chapter 9.2)
Martin Bertau	TU Bergakademie Freiberg (Chapter 9.3)
Angelika Brückner	Leibniz-Institut für Katalyse e. V. (Chapter 6)
Karsten Büker	ThyssenKrupp Industrial Solutions AG, Dortmund (Chapter 8)
Dana Demtröder	DECHEMA e.V., Frankfurt ( <b>Editorial work</b> )
Olaf Deutschmann	KIT – Karlsruher Institut für Technologie (Chapter 4)
Barthel Engendahl	GFBiochemicals (Chapter 9.2)
Roger Gläser	Universität Leipzig (Chapters 1, 2, 5, <b>Editorial work</b> )
Wolfgang Grünert	Ruhr-Universität Bochum (Chapter 6)
Jan-Dierk Grunwaldt	KIT – Karlsruher Institut für Technologie (Chapter 6)
Martin Hartmann	Universität Erlangen-Nürnberg (Chapter 2, 6)
Olaf Hinrichsen	TU München (Chapter 3)
Stefan Kaluza	FhI für Umwelt-, Sicherheits- und Energietechnik UMSICHT, Oberhausen (Chapter 10)
Frerich Keil	TU Hamburg-Harburg (Chapter 7)
Elias Klemm	Universität Stuttgart (Chapter 8)
Ulrike Krewer	TU Braunschweig (Chapter 9.4)
Sven Kureti	TU Bergakademie Freiberg (Chapter 8)
Walter Leitner	MPI für Chemische Energiekonversion and RWTH Aachen (Chapter 9.2)
Andreas Liese	TU Hamburg-Harburg (Chapter 9.3)
Roland Marschall	Universität Gießen (Chapters 2, 9.4)
Martin Muhler	Ruhr-Universität Bochum (Chapter 3, 6)
Mehtap Özaslan	Universität Oldenburg (Chapter 9.4)
Karsten Reuter	TU München (Chapter 7)
Marcus Rose	TU Darmstadt (Chapter 9.1)
Frank Rosowski	Technische Universität Berlin, BasCat UniCat BASF JointLab (Chapter 9.1)
Jörg Sauer	KIT – Karlsruher Institut für Technologie (Chapter 9.1)
Andreas Schmid	Helmholtz-Zentrum für Umweltforschung GmbH – UFZ, Leipzig (Chapter 9.3)
Stephan Schunk	hte GmbH, Heidelberg (Chapters 1, 2, 5, 6, 10, <b>Editorial work</b> )
Ferdi Schüth	MPI für Kohlenforschung, Mülheim (Chapter 10)
Peter Strasser	TU Berlin (Chapter 9.4)
Felix Studt	KIT – Karlsruher Institut für Technologie (Chapter 4, 7)
Annette Trunschke	Fritz-Haber-Institut der MPG, Berlin (Chapter 9.1)
Peter Wasserscheid	Universität Erlangen-Nürnberg (Chapter 9.2)
Nicole Wilde	Universität Leipzig ( <b>Editorial work</b> )

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**DECHEMA**  
Gesellschaft für Chemische Technik  
und Biotechnologie e.V.  
Theodor-Heuss-Allee 25  
60486 Frankfurt am Main

Phone: +49 69 7564-0  
Fax: +49 69 7564-117  
Email: [info@dechema.de](mailto:info@dechema.de)

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