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CATALYSIS

An interdisciplinary key technology for a sustainable economic development

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The present document is a translation of the German Catalysis Research Roadmap. This Roadmap addresses the Catalysis Area in Germany. The European Dimension of Catalysis is treated in the „Science and Technology Roadmap on Catalysis for Europe" of EFCATS (https://efcats.org/Resources/Highlights+in+Catalysis/Science+and+Technology+Roadmap+on+Catalysis+for+Europe.html).

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Summary

Catalysis is a field of knowledge and research that we encounter in all areas of daily life. It plays a crucial role in all value chains, being used in about 80% of all chemical processes. Catalysis is therefore also a technological basis for meeting future challenges on a global scale. In the fields of energy transition, world nutrition, emission reduction, safeguarding water quality and in many other fields, the development of efficient catalysts is essential.

Catalysis research stands out as an interdisciplinary field that benefits from many related disciplines and directly provides essential contributions to them. For example, materials science for the development of new stable catalyst materials, engineering sciences for the development of new reactors and reactor concepts, and biology for enzyme research all play a crucial role in advancing the field of catalysis.
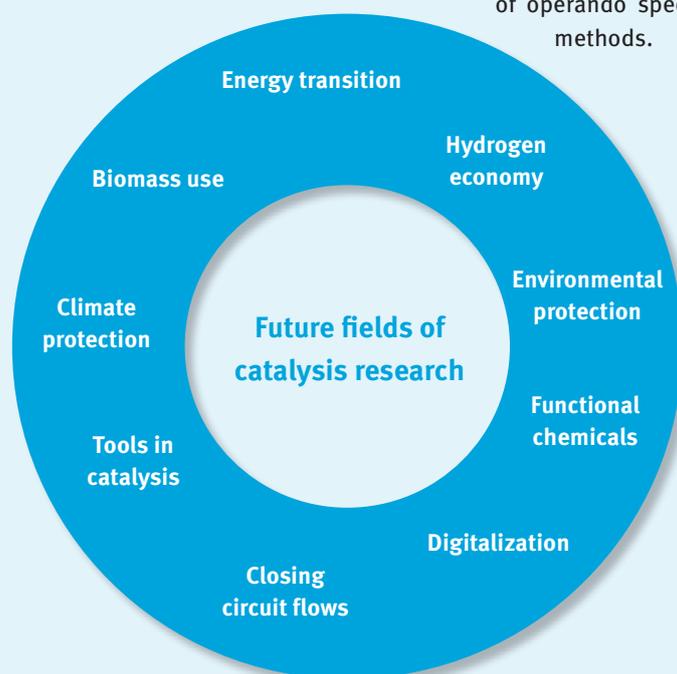
Catalysts will continue to be developed further in the coming years. Only through this further development are chemical conversions possible for opening up new raw materials and for providing targeted value-added products. In addition, efficient and energy-saving conversions are of great importance for the future. In this roadmap, these trends are presented in six topic areas. These topics represent the wide range of German catalysis research and are structured on the basis of the applications of catalysis.

For example, the energy transition and the hydrogen economy play a prominent role in the development of catalysts. Catalysis research thus lays an essential foundation for the success of the energy transition. The conversion of energy production as well as the changing raw material base from fossil to sustainable and renewable resources such as the use of biomass, plastic recycling streams or CO_2 as substrate base pose completely new challenges to catalysis and determine future research and development.

Emissions to air, water and soil are critical for climate and environmental protection. Here, catalysis is essential for reducing and preventing emissions into the environment. One focus is on water treatment and the treatment of exhaust gas streams, also for future mobility concepts.

Modern society depends on highly specialized functional chemicals, such as weight-reduced components, highly effective medicines, food additives and efficient fertilizers. Innovative catalysts pave the way for producing these chemicals sustainably and in closed raw material cycles.

Digitalization is a topic that also plays an enormous role in catalysis research. To develop new catalysts and understand their functional principles as well as to apply catalysts, it is essential to use a variety of tools. These range from innovative reactors to investigative methods of operando spectroscopy and theoretical methods.

Future fields of catalysis research

- Energy transition
- Hydrogen economy
- Environmental protection
- Functional chemicals
- Digitalization
- Closing circuit flows
- Tools in catalysis
- Climate protection
- Biomass use

Introduction

In order to meet global challenges with sustainable developments, the United Nations has defined 17 global Sustainable Development Goals. As an interdisciplinary cross-sectional technology and a key scientific discipline, catalysis can make significant contributions to several of these goals. These include, for example, Goal 7 "Affordable and clean energy" and Goal 12 "Sustainable consumption and production". These are directly related to catalytic technologies such as electrocatalytic water splitting for the production of hydrogen using solar and wind energy or the sustainable synthesis of fuels from carbon dioxide or of functional chemicals from renewable raw materials. The goals of closed material cycles or a carbon-neutral chemical industry will also not be achievable without catalysis. However, world nutrition, health, clean water and climate-neutral action are also areas in which catalysis is essential and will become increasingly important in the future. All these topics are covered in this roadmap and the role of catalysis is addressed.

Catalysis has long played a central role in many industrial application fields and production areas. It will continue to assert and expand its importance in and for industry as a key technology for the production of materials and chemicals in the future. Driven by changing raw material availability, the requirements of the energy transition or the contributions to climate protection, catalysis is also evolving. Thus, beyond the conventional disciplines of catalysis on surfaces, molecular catalysis and biocatalysis, further sub-disciplines are emerging, such as electro- and photocatalysis or organocatalysis. How highly dynamic the research field is, also in Germany, is shown not least by the Nobel Prize in Chemistry, which was awarded last year to Benjamin List and David MacMillan for the development of asymmetric organocatalysis. And a quote from Benjamin List sums up the importance of catalysis in clear words: "Catalysts are used in everything that chemists do with molecules. It is probably the most important technology of mankind."[1].
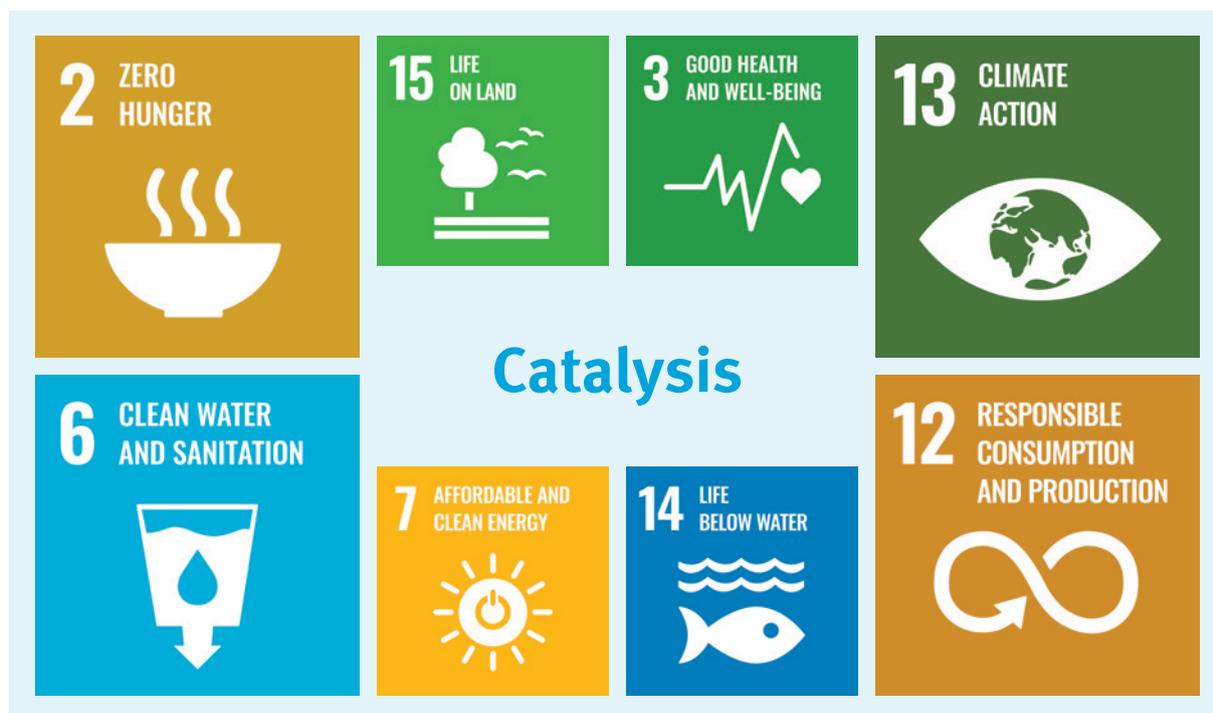

Figure 1: Sustainable Development Goals that depend significantly on the development of catalysts[2].

1   Die Zeit, 09.12.2021, No. 51, S. 19-21
2   https://sdgs.un.org/goals

Catalysis also owes its importance to its close links with several neighboring disciplines. There is a mutually beneficial, synergistic relationship with these disciplines. Thus, on the one hand, an understanding of the mode of action of catalysts is required in biology, materials science or engineering, for example, while on the other hand, knowledge of the biological and engineering framework and conditions of use is also an essential basis for understanding and utilizing the effect of catalysts in their respective fields of application. An application-oriented, resource- and time-efficient further development of catalysts and catalytic processes must take this interdependence of research and technology fields into account and integrate it into future developments.

The scientific spectrum of catalysis research ranges from the fundamental understanding of catalyst action at the atomic and molecular level, to dynamic structures of solids and enzymes, to complex reactors and processes over several orders of magnitude of time and length scales. Despite the diverse and fundamental advances in understanding catalytic action, for numerous applications of catalysts in industrial practice, reliable prediction of their functional properties remains a challenging goal.

In order to promote the development of catalysis against the background of the current challenges for sustainable development, this Roadmap of German Catalysis Research describes the medium-term needs for research

areas and goals with a view to longer-term visions. It is addressed to the German catalysis community, but in particular also to those organizations that promote and fund research in the field of catalysis.

The roadmap is divided into the following six chapters:

» Energy transition and hydrogen economy
The first chapter deals with the role of catalysis in the energy transition and the hydrogen economy. As a key technology, catalysis plays a central role in the widespread use of renewable energies in all sectors. Catalysts can be used to convert sustainable but volatile electrical energy sources, such as wind or solar energy, into chemical energy. Catalysis thus enables on the one hand the storage of these volatile forms of energy, e.g. in hydrogen or other chemical energy carriers (e-fuels, biofuels, LOHCs, etc.), but also the use of electrical energy in chemical production and for material use.

» From fossil raw materials to a cycle of carbon resources
This chapter describes the development goals in catalysis for a sustainable transformation of today's linear chemical industry with the aim of closed carbon cycles. Catalysts are essential to enable selective chemo-, bio- or even electrocatalytic reactions in the face of dynamically changing resources. Fossil

Energy transition and hydrogen economy

From fossil raw materials to a cycle of carbon resources

Climate and environmental protection

Sustainable functional chemicals

Digitalization in catalysis

Experimental and theoretical tools for catalysis research
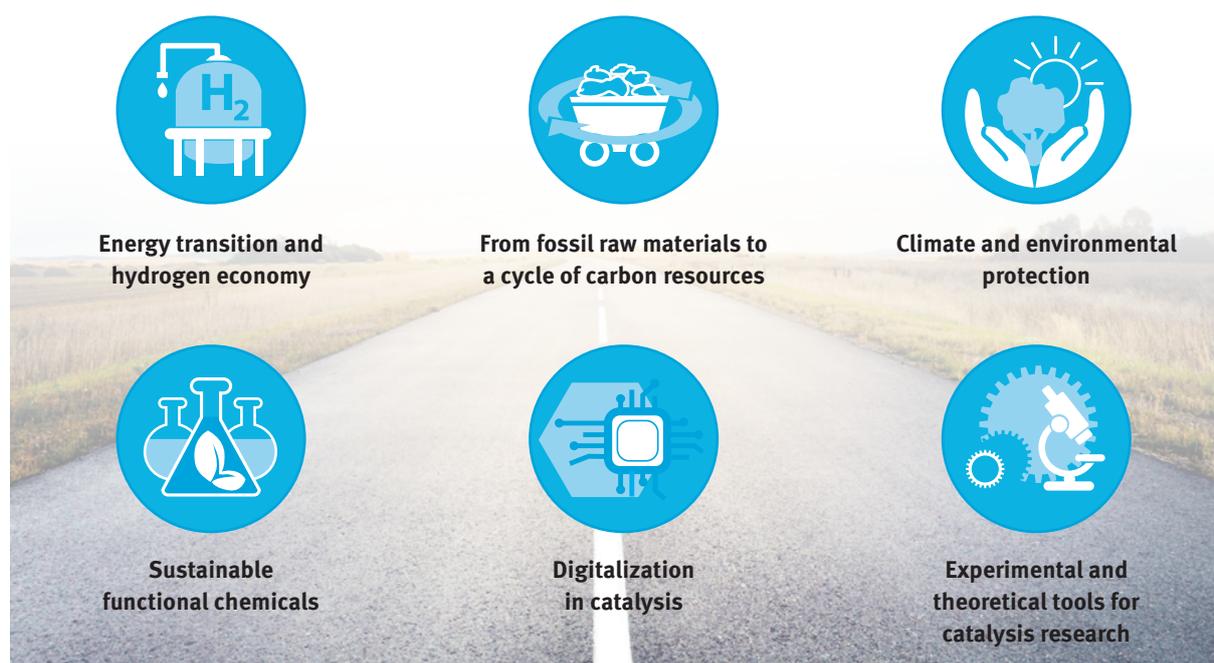
Figure 2: The topics of the roadmap of German catalysis research.

feedstocks will be replaced as carbon sources by renewable carbon sources such as CO_2 and biomass as well as recycling streams, e.g. in the form of plastics. Catalysts make it possible to selectively convert raw materials that are highly diverse in functionality and reactivity and to develop efficient value chains.

» Climate and environmental protection

Catalysis makes a significant contribution in processes to keep air, water and soil clean and to protect the environment. It is firmly established in technical applications for reducing emissions from mobile and stationary combustion sources. For example, catalysts are produced and used in large quantities in the field of automotive exhaust gas purification. The increasing introduction and use of more climate-friendly mobility concepts such as methane, hydrogen, e-fuel and hybrid engines is leading to new challenges, which are detailed in this chapter.

» Sustainable functional chemicals

This chapter summarizes important fields for the sustainable production of functional chemicals. For example, the importance of catalysis for plastics, pharmaceuticals, feed and food, and fertilizers is presented. Applications of these chemicals include specialty polymers in lightweight construction or food and feed products in which vitamins, flavorings, feed supplements or food colorants are used in large quantities. Another important area is crop protection products and pharmaceuticals.

» Digitalization in catalysis

This chapter describes a fundamental rethink in the handling of data in catalysis research and development, especially in the context of chemical engineering and process technology. Digital transformation is a core challenge. It requires a contemporary and future-oriented approach to digitalization. The paradigm shift to "digital catalysis" is to be realized along the data value chain, which is oriented parallel to the real value chain from molecules to chemical processes.

» Experimental and theoretical tools for catalysis research

The final chapter covers the wide range of methods and tools used in all subfields of interdisciplinary catalysis. Methods and procedures from chemistry, materials science and biology, artificial intelligence methods and computer science help in the search for new catalysts by developing data-based models.

The structure of the roadmap is thus divided into topics in which catalysis plays a decisive role. An introductory statement and a vision of the next ten years precede each chapter. The content and significance of the topics are described in subchapters, followed by a concise formulation of the medium-term research needs. This shows what challenges exist in the respective topic area in order to be able to ensure the success of catalysis research and its further development in the future.

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1 Energy transition and hydrogen economy
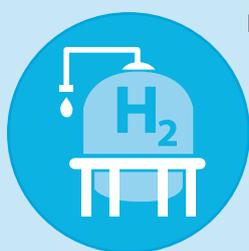
In the energy transition and hydrogen economy, catalysis as a key technology plays a central role for the use of renewable energies in all sectors. Catalysts can be used to convert sustainable but volatile electrical energy sources, such as wind or solar energy, into chemical energy. Without catalysts, this usually does not or only very inefficiently take place. Catalysis enables on the one hand the storage of these volatile forms of energy, e.g. in hydrogen or other chemical energy carriers (e-fuels, biofuels, LOHCs, etc.), but indirectly also the use of electrical energy in chemical production. Catalysts are also key components in the recovery of stored chemical energy as electrical energy, e.g. within fuel cells. In general, issues of the energy transition, the hydrogen cycle and the use of electrical energy are closely linked to the issues of raw materials and the circular economy or the carbon cycle addressed in Chapter 2.

1.1 Water electrolysis

Vision

» Catalysts enable the efficient production of green hydrogen.

» Different water electrolysis technologies allow optimized hydrogen production depending on local conditions and requirements.

» Economically competitive green hydrogen enables the storage of renewable energy and the defossilization of numerous industries.

» The catalysts themselves use the material resources responsibly.

» The economics of electrolyzers are increased by alternative anodic reactions instead of oxygen production.

Green hydrogen plays a key role in the energy transition. The electrolysis of water makes it possible to convert fluctuating renewable electrical energy into hydrogen. This has the highest mass-specific energy density, can be produced and transported as a gas, and is the starting point for numerous technologies for storing renewable energies and defossilizing various sectors. Catalytic water electrolysis is therefore of particular relevance. There is still a great need for research and development in all electrolyser technologies. These include alkaline electrolysis (AEL), anion exchange membrane electrolysis (AEM-EL), proton exchange membrane electrolysis (PEM-EL) and solid oxide electrolysis (SOEC). The different types of electrolysis and specific catalytic issues are briefly introduced below.

Proton Exchange Membrane Electrolysis (PEM-EL)

PEM electrolyzers also called acidic low-temperature electrolyzers achieve a high power density and guarantee high dynamics in operation. These properties qualify the PEM especially for decentralized applications with frequent on/off cycles and the technology is currently on the verge of commercialization. However, the acidic environment caused by the sulfonic acid groups in the polymer membrane and the high potentials significantly limit the choice of (catalyst) materials. Platinum-based catalysts are used for hydrogen evolution at the cathode, while iridium- or ruthenium-based catalysts are used for oxygen evolution at the anode. Iridium oxide is significantly more stable than ruthenium oxide and is currently the material of choice for commercially avail-

able catalysts. To achieve widespread implementation on a gigawatt scale, a reduction in anode loading from the current level of about 2 mg cm^{-2} to 0.05 mg cm^{-2} is required to achieve an iridium-specific performance of 0.01 g_{Ir} kW^{-1}. This can only be achieved if precious metal quantities are drastically reduced through further R&D efforts. One approach is atomically thin films of the noble metals, which are deposited on suitable core materials. Here, mixed oxides between catalyst and support material must be avoided to guarantee sufficient stability. Other approaches use alloys and surface modifications to increase the specific activity per mass of noble metal. In addition to reducing the amount of precious metal, stability must also be increased. Here, the active components must be considered together with the carrier materials. As carriers, which combine electrical conductivity with stability under the harsh reaction conditions, the so-called "valve metals" or their oxides consisting of Ti, Zr, Ta, Nb, or Sn are mainly considered. In particular, Sn-based materials doped with Sb or F show the necessary conductivity, but still struggle with a lack of stability.

Alkaline low temperature electrolysis

Two technologies can be distinguished in alkaline electrolysis: Alkaline electrolysis with concentrated KOH as electrolyte (AEL) and, analogous to PEM-EL, anion exchange membrane electrolysis (AEM-EL). The catalytic materials used are similar in both technologies. Nickel-based catalysts are used on the cathode and anode, sometimes with precious metals added to improve kinetics. In principle, AEM-EL combines the advantages of a KOH and PEM system: low-cost catalysts, high stability, and the ability to operate at higher pressures and current densities. The challenges lie in water management and in the stability and conductivity of the new alkaline membranes. Despite the use of non-critical materials, activity and stability still need to be enhanced for the catalysts. Structured catalysts for optimized gas/liquid mass transport are one possibility towards this challenge. Especially for the broad GW application of electrolysis, even small increases in efficiency are relevant. Ternary and multinary material combinations, often with nickel and iron, catalyze water oxidation with low overpotentials and higher stabilities, especially at high current densities, than e.g. pure nickel. In addition, the active surface area plays a major role, which can be achieved, for example, by "Raney-Ni" like structures. In general, scalable and cost-effective fabrication strategies and activation protocols need to be found to achieve highly active and stable catalysts. Since an aqueous electrolyte is used in the AEL, the technology is well suited to use

alternative reaction at the anode instead of oxygen release. This can reduce the energy requirements of the electrolyzer and can produce additional valuable materials. One challenge is to adapt the catalysts for the new anode reactions to the operating conditions and current densities of water electrolysis.

High-temperature electrolysis

Solid oxide electrolysis cells (SOECs) have recently emerged as highly efficient for hydrogen production. They are operated at high temperatures of 500 - 950 ºC with oxygen ions as charge carriers in a ceramic electrolyte. Due to the high operating temperature, there is no risk of poisoning by CO and SOEC can also be used for co-electrolysis, i.e. the simultaneous conversion of CO_2 and H_2O into synthesis gas (CO, H_2). For high-temperature electrolyzers, it is particularly interesting to note that the Gibbs free energy change, or the electrical energy demand of the system, decreases with increasing temperature, while the product of temperature and entropy change, or the thermal energy demand, increases. Thus, a portion of the total energy demand can be provided in the form of heat. High-temperature operation is therefore also favorable from the point of view of kinetics and electrolyte conductivity. In principle, SOEC can be operated in a thermoneutral, exothermic and endothermic mode, which is of great interest for thermal coupling with *downstream* processes such as methana-

tion. ZrO_2 and other oxides with high melting temperature and strength, usually stabilized with Y_2O_3 (YSZ), are used as oxygen ion conductors. Lanthanum strontium manganate (LSM) is the most common anode material, and in the cathode YSZ is doped with Ni. Challenging is still the aging of the cells caused by thermal stresses, especially delamination. More intensive high-temperature proton conductors have recently been investigated as alternatives. Compared to other electrolytic cells, the SOEC shows a very high efficiency, but cannot tolerate such high dynamics in load behavior as e.g. a PEM. von großem Interesse ist. Als Sauerstoff-Ionenleiter werden ZrO_2 und andere Oxide mit hoher Schmelztemperatur und Festigkeit, meist mit Y_2O_3 stabilisiert (YSZ), eingesetzt. Lanthan-Strontium-Manganat (LSM) ist das häufigste Anodenmaterial, in der Kathode wird YSZ mit Ni dotiert. Herausfordernd ist immer noch die durch thermische Spannungen verursachte Alterung der Zellen, insbesondere durch Delamination. Als Alternativen wurden jüngst auch intensiver Hochtemperatur-Protonenleiter untersucht. Gegenüber anderen Elektrolysezellen zeigt die SOEC einen sehr hohen Wirkungsgrad, kann aber keine so hohe Dynamik im Lastverhalten wie z. B. eine PEM tolerieren.
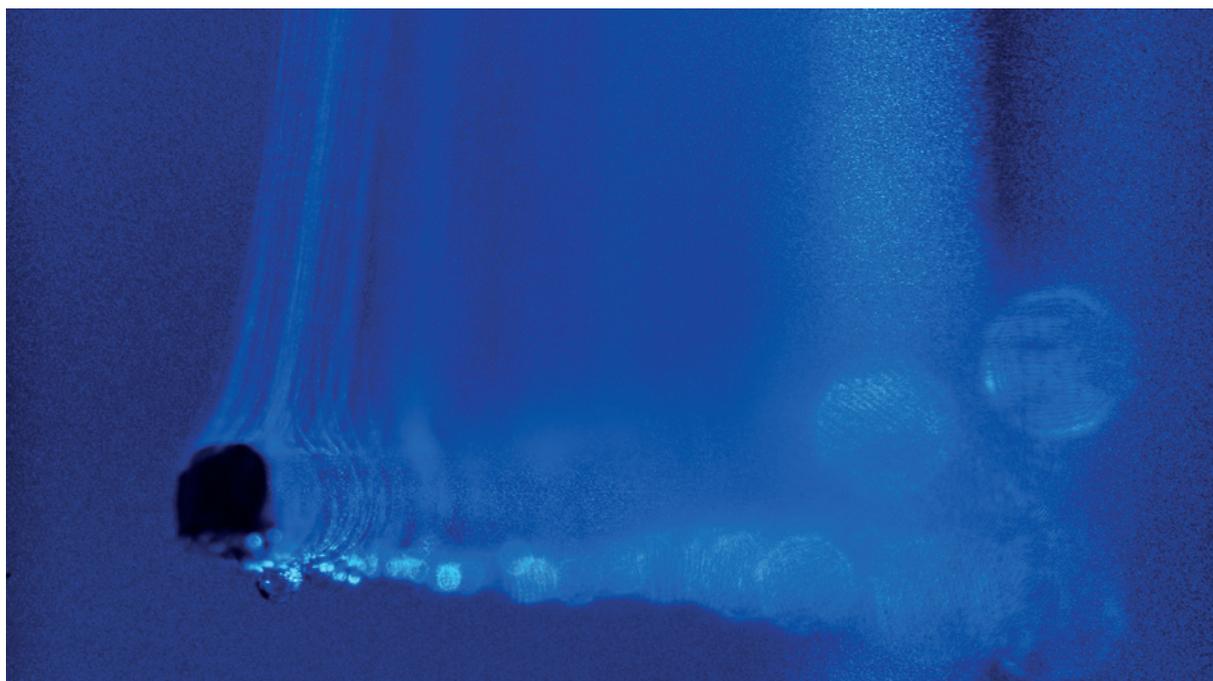

Figure 3: Path line visualization of bubble flow by long time exposure in alkaline water electrolysis on a nickel catalyst wire.
(© Max Greifenstein, Andreas Dreizler, TU Darmstadt)

1.2   E-fuels and hydrogen storage

Hydrogen has a high mass-based energy density, but its volumetric energy density is low and, in general, gases are more difficult to store than liquids or solids. Especially for long-term storage or applications where only a small additional volume is available for storage, hydrogen-based storage molecules with high volumetric energy density and good manageability are more suitable. These chemical storage media can be divided into three categories: I) storage molecules from which hydrogen is released again; II) fuels (e-fuels) which release the energy content introduced by hydrogen in combustion reactions; III) chemicals which are used materially in the chemical industry, where the energy content of the hydrogen is used to defossilize production.

The diversity of chemical storage molecules is not a disadvantage here, but opens up application-specific use of the stored energy and enables the coupling of the energy and chemical sectors. Catalysis has a key role to play here, as it enables sufficiently large storage and retrieval rates and minimal energetic losses. However, the great

strength of catalysis is its ability to selectively produce a wide range of different storage molecules. The need for research and development thus also extends across the breadth of possible application scenarios and storage molecules.

Hydrogen carrier

The most prominent examples of storage molecules that may become relevant depending on application size, region, and the policy framework are ammonia and its derivatives, so-called "liquid organic hydrogen carrier" (LOHC) systems, alcohols, and formic acid.

Ammonia (NH_3) is gaseous under standard conditions and is of interest as a storage molecule because it can be liquefied (20 °C) at a pressure of 9 bar. Its combustion produces mainly nitrogen and water as exhaust gas; a CO_2-free combustion cycle can thus be realized. Nitrogen oxides formed in small amounts can be very well reacted off by catalysis in emission control. NH_3 is currently produced on a scale of ›100 million t/a using the Haber-Bosch process. In this process, the gases nitrogen and hydrogen react at about 200 bar and 450 °C on an iron catalyst. One challenge is to increase the activity of the catalysts in order to take advantage of the more favorable equilibrium situation at lower temperatures and lower pressures (see also section 4.4 Fertilizers). Currently, the electrochemical electrolysis of N_2 to NH_3 is also being intensively investigated, although it is still unclear whether research can provide sufficiently active, selective and stable catalysts.

Formic acid and formates can be produced from CO_2 under much milder reaction conditions than ammonia. However, the energy density is lower. In addition to the established two-step process for the production of formic acid, formates can be obtained in high selectivity via various catalytic processes, in particular chemocatalytic, biotechnological or even electrocatalytic CO_2 reduction (see also CO_2 and water co-electrolysis in Chapter 1.4). The selectivity and stability of the electrocatalysts for high current densities and thus space-time yields must be further increased here. Furthermore, formic acid as well as other molecules electrocatalytically accessible from CO_2 offer an excellent interface for (bio)technological synthesis (see also chapter 1.4.).

The storage molecules described are usually composed of hydrogen and other gaseous components such as CO, CO_2 or N_2 and are broken down again into these components or the combustion products when hydrogen is released. In contrast, in the so-called LOHC systems

(liquid organic hydrogen carrier), the hydrogen is bound to mostly aromatic or heteroaromatic carrier liquids in a catalytic hydrogenation reaction and released again by the corresponding reverse reactions. The carriers are liquid in the unloaded and loaded state and hydrogen is the only gas component, which simplifies handling. Exothermic hydrogenative loading of the storage materials takes place on heterogeneous Ni, Ru,Pd or Pt catalysts at the pressure level of hydrogen production by electrolysis (15-30 bar) at 80 to 320 °C. Endothermic dehydrogenation for hydrogen release is typically carried out at hydrogen pressures of up to 5 bar and temperatures between 250 and 350 °C on supported platinum-containing catalysts. Direct LOHC fuel cells represent a particularly promising variant of hydrogen release and direct utilization, which, however, still requires further research and development work in the field of electrocatalysis.

E-Fuels

Synthetic hydrocarbons can be produced primarily via Fischer-Tropsch synthesis (FTS), methanol synthesis, and methanation by reacting hydrogen with CO or CO_2. All three processes are established on a large scale for classical synthesis gas. It can be sustainably produced in the future by gasification of waste and biomass or by thermal-catalytic or electrocatalytic conversion of CO_2 and H_2O and used in the established processes. In order to circumvent the disadvantages of upstream syngas

production, such as the unfavorable equilibrium position or incomplete utilization of CO_2, there is currently a great need for R&D in the direct utilization of CO_2 and CO_2/CO mixtures, especially for the catalysts used. Synthesis gas also forms the bridge to many material utilization paths (see Chapter 2.3).

Two different catalyst classes are distinguished in FTS: Low-temperature FTS performed on co-catalysts (20-40 bar, 200-230 °C) results in longer-chain, waxy products that are subsequently upgraded to synthetic diesel or kerosene. Fischer-Tropsch synthesis (FTS) at high temperatures (Fe catalysts, 20-40 bar, ›300 °C) tends to target short-chain hydrocarbons and olefins as chemical feedstocks. When using Fe catalysts, CO_2 or CO_2/CO mixtures can be used directly due to the activity for the water-gas shift reaction. However, the activation of the iron oxide as well as the subsequent deactivation at different mixing ratios still pose a challenge. An alternative to FTS with CO_2 is the synthesis of methane using mainly Ni catalysts, which are characterized by acceptable cost and high methane selectivity. Methanation is carried out at elevated pressure (› 10 bar) and - depending on the reactor concept – at different temperatures (250 - 600 °C). For thermodynamic reasons, a single-stage conversion can only be achieved at low temperatures. Both variants of FTS as well as methanation are strongly exothermic, which poses additional challenges to the temperature

Figure 4: bioliq® plant at the Karlsruhe Institute of Technology for the production of BTL (biomass-to-liquid) fuels via synthesis gas, DME and OME. (© KIT)

stability and thermal conductivity of the catalysts. Continuous catalysts such as monoliths, foams or 3D-printed structures are concepts to significantly improve heat dissipation.

In addition to FTS and methanation, the synthesis of methanol and its derivatives such as dimethyl ether (DME) represents the third pillar in the synthesis of e-fuels from CO-, but also CO_2-rich synthesis gas. Both methanol and DME are not currently used directly as fuels in Europe. However, methanol is one of the most important building blocks of the chemical industry. Hydrocarbons (kerosenes, olefins, aromatics) can be produced from methanol and DME by catalyzed oligomerization reactions for use as building blocks in the chemical industry, but also as gasoline, diesel fuel or kerosene. Methanol and DME can serve as intermediates for the production of new synthetic fuels such as oxymethylene ether (OME).

When fossil raw materials such as natural gas or coal are used, CO-rich synthesis gas is used for the production of methanol and DME. For this purpose, catalysts and reactor configurations have been tested on a very large scale for years. State-of-the-art for methanol synthesis are copper-based catalysts with the components copper-zinc-alumina (CZA). Solid acid catalysts such as γ-Al_2O_3, ZSM-5 or ferrierite are used as catalysts for the further reaction of methanol to DME. The conversion of CO_2 with hydrogen to methanol or DME is possible with currently known catalysts, but only comparatively low conversions at high pressure are achieved and the long-term stability in the presence of water vapor is lower. To increase process efficiency, active and stable catalysts and new reactor configurations are needed with which high CO_2 conversions can be achieved under thermodynamically favorable conditions with a low proportion of synthesis gas recirculation.

OMEs have combustion properties similar to diesel fuel. Due to their structure, soot formation during combustion is drastically reduced compared to diesel fuel. The application properties can be adapted by adjusting the chain length of the OME. The state of the art for production is low-energy-efficient multistage process chains. To increase process efficiency, multifunctional catalysts and processes are needed which, starting from CO, CO_2 lead directly to OME components with high yields.

Research needs

» Research should cover all realistic possibilities and target molecules for specific application scenarios in each case.

» Depending on the process or storage molecule, selectivity and stability must be increased in catalyst research. Approaches to increase activity are particularly interesting to lower temperature levels for equilibrium-limited exothermic reactions or to equalize temperature levels in the heat network.

1.3 Fuel cells

Vision

» Various fuel cell technologies allow the dynamic or static provision of electricity, in both stationary and mobile applications.

» Catalysts enable minimization of losses and significantly higher efficiency of fuel cells compared to combustion.

The fuel cell converts the energy contained in chemical storage molecules into electrical energy. Depending on the type of fuel cell, various fuels can be considered, which can be used for different applications such as in the transportation sector, stationary, for emergency power supply or in small mobile devices. The main challenges of the fuel cell are 1) to reduce the cost and the necessary amount of critical materials, 2) to increase the power output and 3) to increase the stability of the materials used. At the heart of the fuel cell are catalysts, which must meet these challenges. Depending on the fuel cell type, different catalytic materials are used.

Low temperature proton-exchange membrane fuel cell

The preferred fuel cell technology in the transportation sector is the polymer electrolyte fuel cell (PEM-FC). The advantages compared to battery-based systems are the high gravimetric power density, long range, fast

charging or filling time and easy integration into existing systems/infrastructure. In addition, decoupling of power provision and energy storage is possible, so that large energy storage volumes are possible with the same material input. The low operating temperature of about 80 °C enables fast start-up and shorter warm-up time. These strengths make PEM-FCs an important alternative to battery-powered mobility, especially for high power requirements and long ranges (e.g. vans, trucks, buses, trains, ships). However, the system costs of PEM-FC are still high compared to classic combustion engines. In particular, the catalysts, which have so far been exclusively precious metal-based, represent a cost driver. In the mobile sector, Pt-based catalysts show the highest performance on the anode and cathode side. Since the amount of platinum used on the anode side (about 0.05 mg cm^{-2}) is small compared to the cathode, the R&D focus is increasingly on the cathodic oxygen reduction reaction. In recent years, there have been major efforts to reduce the amount of platinum on the cathode from 0.4-0.8 mg$_{Pt}$ cm^{-2} to about 0.1 mg$_{Pt}$ cm^{-2}, thus coming within the range of precious metal amounts already used and recycled in automotive exhaust catalysts. To achieve the same power densities, the Pt-based catalysts still have to become more active in terms of platinum mass. This can be achieved, for example, by alloying the platinum, using so-called shape-controlled structures that contain highly active platinum surfaces to the greatest possible extent, improving the surface-to-volume ratio in core-shell catalysts (Figure 4) or modifying the surface with ionic liquids. However, degradation processes and activ-
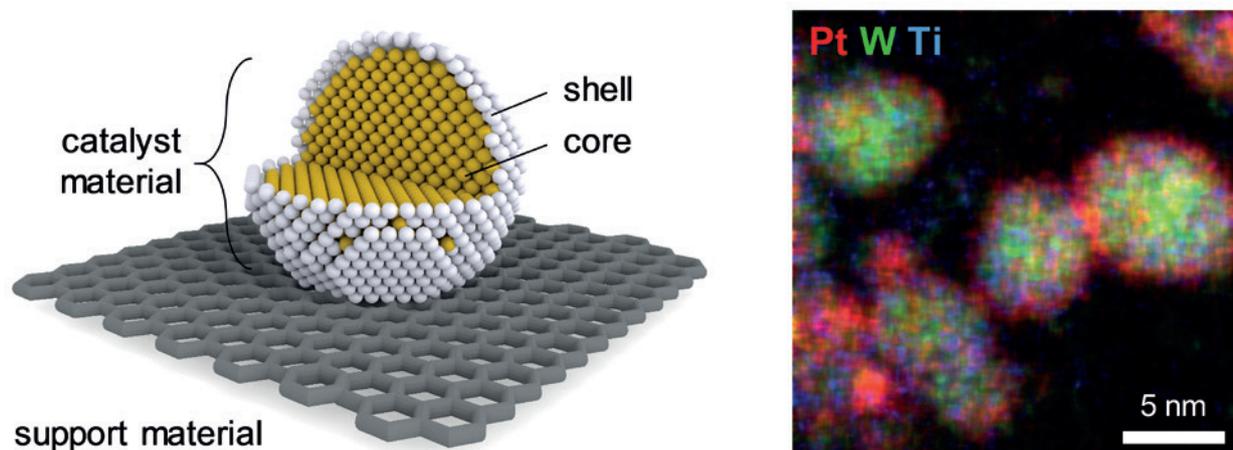

Figure 5: Left: Concept for reducing the amount of precious metal using cores made of readily available materials covered with a thin shell of precious metal. Right: STEM-EDX image of selected core-shell particles with platinum as shell material and a tungsten/titanium mixed carbide as core material. (© Marc Ledendecker)

ity degradation at low platinum loadings and high current densities are still a challenge to produce high-performance electrodes. In addition, the accessibility of the active sites at low platinum loading must be ensured. Here, a deep understanding of the interplay between support material, catalyst and ionomer is necessary.

In addition to the possibilities for platinum reduction via an appropriate "catalyst design" of the platinum, the substitution of platinum by non-critical elements is the subject of intensive R&D activities. In this context, the group of metal-nitrogen catalysts in particular plays an important role, and although these do not yet reach the performance densities of Pt-based catalysts, great progress has been made in recent years in terms of activity and stability. However, it is becoming apparent that activity and stability are oppositely related and future research urgently needs to develop new stabilization strategies. Possible causes of degradation are the dissolution of metal components from the catalyst, high formation rates of hydrogen peroxide and associated oxidation processes, and corrosion of the carbon support. In the case of the most active catalysts in this group, the iron-nitrogen catalysts, this can lead to a Fenton reaction and destruction of the ionomer/membrane. One approach to increasing stability is to significantly reduce the minor phases while simultaneously increasing the density of the active sites. A key role here is also played by the carbon used, which must combine a high surface area with a stable graphitic structure.

Direct methanol fuel cell

The direct methanol fuel cell (DMFC) is mainly used in the portable sector and achieves efficiencies of 30-40 %. One advantage is the easier handling and transport of the liquid methanol, for which the existing (tank) infrastructure can be used. Although the performance of DMFC has been increasing for years, durability needs to be increased and costs reduced. In particular, electrode degradation leads to increased kinetic losses and mass transport losses. The high price and low availability of the catalysts used (usually containing precious metals) are challenges that need to be urgently addressed. The solution strategies are similar to those for PEM-FCs. Especially for the DMFC, noble metal-free metal-nitrogen catalysts are of high interest, since they show significantly lower sensitivity to carbon monoxide and various alcohols.

Alkaline low temperature fuel cell

Alkaline fuel cells (AFCs) can traditionally be operated in a potassium hydroxide solution or using a polymer electrolyte membrane as the electrolyte. Due to the higher pH values, non-noble metal materials can also be used in both cases; however, they do not yet achieve the required current and power densities. Due to the steady improvement of membrane materials in recent years, the alkaline anion exchange membrane fuel cell (AEMFC) is becoming increasingly important. The design is based on PEM fuel cells. Instead of an acidic membrane, alkaline membranes are used. Open questions concern in particular membrane conductivity and stability as well as water management and carbon dioxide tolerance. Another challenge is to identify non-critical catalyst materials that have the necessary activity and stability to reduce overall costs.

Solid oxide fuel cell

The high temperature fuel cell (solid electrolyte cell, SOFC) has been studied for decades and is the reverse process of the SOEC described in Section 1.1. The same low-cost ceramic materials and nickel are used, and tubular and planar, electrolyte- and anode-supported designs are available. SOFCs also operate at a relatively high temperature (600-1000°C), which has both advantages and disadvantages for their use. Advantages of SOFCs are high efficiency, tolerance to fuel impurities and fuel flexibility, so in principle hydrocarbons can also be used as fuel (natural gas, methanol). With reversibly operated SOEC/SOFC processes, power-to-power efficiencies of up to about 70 % are possible. Disadvantages are the lack of dynamics in contrast to PEM-FC, which more or less excludes dynamic applications such as in vehicles, and the susceptibility of the ceramics to thermal stresses as well as the demanding sealing technology. The SOFC currently seems to be experiencing its large-scale industrial breakthrough, initially in the field of decentralized power plant technology and power supply as an auxiliary power unit, but interest in the development of SOFC systems for mobile and portable applications is now also increasing. SOFC systems are often still being linked with conventional technologies such as gas burners and turbines, and in the long term probably also with battery technologies. Coupling with biomass gasification plants is also interesting.

Molten carbonate fuel cell

Molten carbonate fuel cells (MCFC), similar to SOFCs, reach significantly higher operating temperatures and operate between 575 °C and 675 °C. They are used in stationary operation or in industrial cogeneration. Lithium and potassium carbonate are used as electrolytes, and non-precious metal catalysts can be used to reduce costs. Due to the high temperatures in the molten salt,

degradation phenomena of the catalysts are among the greatest challenges.

Research needs

» The research concepts for the significant reduction of the amount of precious metal or the complete substitution of the precious metal must be pursued intensively.

» Research concepts to simultaneously increase stability and activity are needed.

» For the SOFC, concepts to reduce material aging caused by thermal stresses and an increase in dynamics are necessary.

1.4 Use of electrical energy in chemical production processes

Vision

» Renewable electrical energy is used to defossilize the chemical industry.

» A portfolio of technologies allows specific products with a low CO_2 footprint to be manufactured economically in a circular economy.

In addition to water electrolysis, which is described in section 1.1, there are other possibilities for using electrical energy in the chemical industry, e.g., for further electrolysis or electrosynthesis processes, for exciting plasmas or for electrical heating. These technologies could cover large parts of the chemical industry's energy needs currently met by fossil fuels with sustainably produced electrical energy, reusing raw materials and saving carbon dioxide emissions. An important basic requirement for realizing potential emission savings is the availability of electrical energy in I) sufficient quantities and II) a cost structure that allows chemicals and fuels to be produced on competitive terms. A particular challenge is the possibility of using temporarily generated "surplus electricity" from renewable sources. The challenges associated with this are to be seen in particular in the area of transient operation management and storage of the chemicals and fuels produced and thus represent important development goals for the application of the technologies. For chemical and fuel production typically designed for continuous operation, this poses new requirements in terms of heat integration and logistics, but above all in terms of catalysts with a high tolerance for dynamic operation. Another key factor in the electrification of chemical and fuel production is the conversion efficiency of electrical to chemical or other forms of energy. Conversion efficiency is particularly low where especially high-energy forms of energy are produced (e.g., plasma). The use of renewable electrical energy, which is currently scarce and comparatively expensive, is therefore particularly suitable for high-value products (such as the production of acetylene based on plasma-assisted processes). Widespread use of renewable electrical energy for fuel production requires promotion and/or corrections in the pricing structure, such as carbon pricing or a "green premium" for products based on non-fossil resources. On the one hand, catalysts are a key to the economic viability of these new processes; on the other hand, the alternative energy input places new demands on the catalysts used.

Co-electrolysis of CO_2 and water

Co-electrolysis of water and CO_2 at the cathode is a promising, albeit very challenging, variant of ordinary water electrolysis. Instead of pure hydrogen, a variety of different carbon-based chemicals and fuels or their precursors can be obtained here depending on the catalyst system, electrode configuration or operating conditions. Starting from CO/H_2 mixtures with a controllable composition from pure hydrogen via synthesis gas to pure CO, mixtures of methane, ethane, ethylene and propylene as well as product streams of various oxygenates such as ethanol, n-propanol, allyl alcohol or acetaldehyde can be produced. An important advantage is considered to be a possible intensification of the process chain towards synthetic fuels, which can offer important efficiency advantages compared to the process chain via conventional water electrolysis. A major challenge is the development of selective cathode catalysts to control competing reaction pathways and thus product selectivity, as well as to increase energy efficiency by reducing overvoltages. The design of the anode and a suitable electrolyte system, as well as an efficient anion exchange membrane, also still pose major challenges for research and development. Current development efforts are investigating both the conventional gas-diffusion electrode design with catholyte and the asymmetric zero-gap, catalyst-coated membrane concept (half-MEA- configuration), which attempts to do without liquid catholyte. Problems such as CO_2 crossover, pH gradients, and carbonate salting out at the cathode need to be solved. Promising new work is aimed at combining electrodialytic CO_2 capture directly with co-electrolysis to realize Direct Air Capture (DAC) of CO_2 and its conversion to chemicals/fuels in a combined electrochemical step.

Electrobiosynthesis

In electrobiosynthesis, electrochemical and microbial catalysis are combined. This combination can be achieved by sequentially carrying out the individual catalytic steps either in-situ, i.e. in the same reaction medium and at the same time, or spatially and temporally separated. Bioelectrocatalysis plays a special role, since here enzymes or preferably microorganisms or microbial communities represent both biological and electrochemical catalysts. All the aforementioned forms of electrobiosynthesis enable the use of a broad portfolio of feedstocks ranging from CO_2 to biomass and waste streams, which are not accessible by purely (abiotic) catalysts. In perspective, the development of an equally diverse product spectrum from fuels to fine chemicals is possible. Thus, electrobiosynthesis as a component of electrobiorefineries can make an essential contribution to sector coupling.

In addition to expanding the portfolio of potential products, the development of demonstrators in an application-oriented environment and the analysis and evaluation of processes are important steps to enable the leap into application. For this, a better understanding of catalysts, e.g., electrocatalysts in a "biocompatible" application environment or catalysts under changing loads, is necessary. In addition, process concepts and, above all, reactors and infrastructure must be developed that meet the requirements of both electrocatalysis and biocatalysis and, at the same time, can be integrated into an industrial environment. Issues concern on the one hand process integration and related control and regulation, but also material durability and resource efficiency. For combined electrochemical-microbial catalysis, optimization of the overall process (rather than optimization of individual steps) is most important. For example, microbial production of organic acids and electrochemical conversion of organic acids to alkanes are individually state of the art, but their effective combination still requires significant development work. This also applies to electrocatalytic synthesis based on CO_2 and biocatalytic upgrading of the resulting products (see also section

1.5). For the bioelectrocatalysts, a significant expansion of the synthesis potential in terms of the possible product portfolio towards high-value chemicals as well as the development of processes for pure and mixed cultures is necessary.

Plasma

One form of direct use of electrical energy is the generation of a plasma, which can be used to activate chemical reactions. Plasmas are already used industrially for the production of certain chemicals. Prominent examples are the production of acetylene in an electric arc via thermal plasma and the production of ozone with non-thermal plasma forms. Other applications of plasma processes include the production of functional materials such as coatings and pigments, and the use of thermal plasma molds to recycle valuable metals.

In contrast to these non-catalyzed plasma processes, plasma catalysis is a young field of research that combines activation via thermal or non-thermal plasma with approaches from the field of catalysis. Here, the catalyst can be placed downstream of the plasma (in the case of arc or microwave plasmas, for example) or integrated into the discharge zone (in the case of barrier discharge
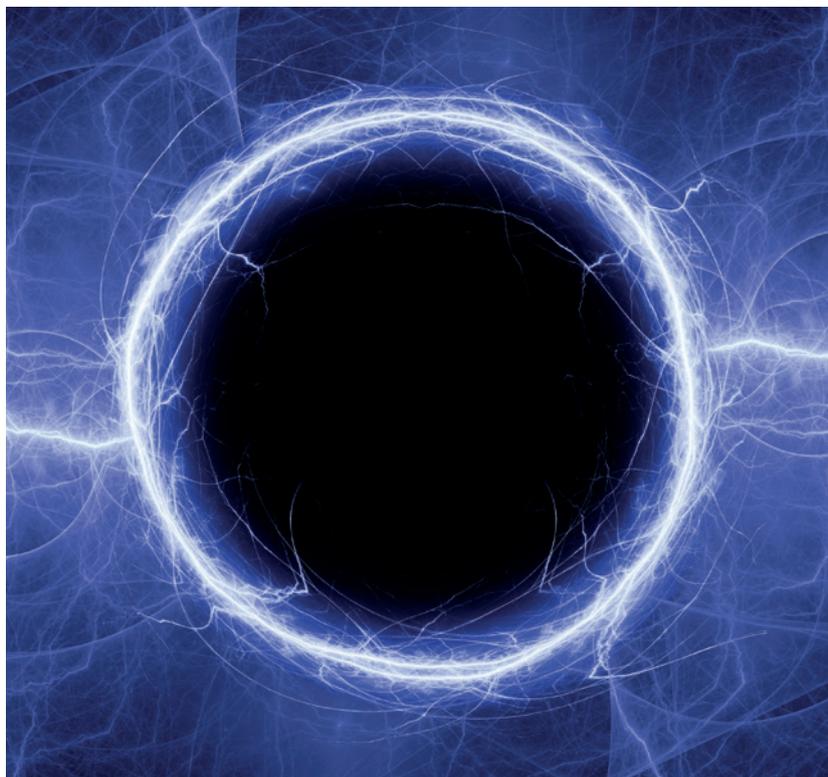

Figure 6: The glow of a flash is caused by the plasma formed. A plasma generated with electrical energy represents a possible future form of activation of chemical reactions. (© Adobe Stock / Martin Capek)

plasmas, for example). While in the first case long-lived intermediates and the high temperature are used for catalysis, in the second case short-lived intermediates are also catalytically converted. In both cases, in addition to increasing energy efficiency, the catalyst can also increase feedstock efficiency through selectivity control.

In addition to the basic research questions of identifying physical and chemical effects of the catalyst and the co-operative effect of plasma and catalysis, efforts to develop optimized reactors and active masses are of interest. One of the challenges with respect to industrial application is the high specific energy requirement to generate thermal or non-thermal plasma forms. This negatively affects the overall efficiency of any process and the associated cost structure of the chemicals or fuels produced. The high energy requirement can be addressed by high conversion efficiency. Two research directions emerge here, one is reactor design and reaction control as an efficiency factor, the other is high target product selectivities which can be addressed by catalyst use.

Electric heating

Another possibility for using electrical energy is to provide reaction heat for endothermic reactions via inductive processes or resistance heating. The advantage here is that electrical energy can be converted into heat with high efficiencies. When using electrical energy to heat catalyst beds, there are different approaches to intensify the electrical heat input: On the one hand, the reactor wall can be directly electrically contacted and used as a heater. This is a pragmatic approach to thermal coupling of electrical energy for a number of applications. However, isolating the reactor from the reactor periphery and avoiding short circuits in reactors and systems made of metal are technically complex. Another promising concept is heat input by directly using the catalyst bed as an ohmic element and resistance heater. This can be particularly advantageous for dynamic operation, since direct heating reduces the thermal mass that must be heated because the surrounding reactor shell does not have to be heated first. The challenges lie particularly in ensuring sufficient electrical conductivity of the catalyst bed and avoiding short circuits. Also important is the avoidance of local temperature peaks; continuously structured catalyst beds based on monoliths or foams appear particularly promising here. From the current point of view, the use of structured and directly heatable catalyst beds produced by 3D printing in particular offers potential that has not yet been exploited. A third method for introducing electrical energy as heat is dielectric heating. In this process, high-frequency electromagnetic waves in the microwave (GHz, wavelength in the centimeter range) or radio wave (MHz, wavelength in the meter range) range are coupled into a solid and converted directly into heat there. Dielectric heating complements the two aforementioned methods in that even electrically non-conductive materials and packed beds can be heated homogeneously and 'from the inside out'. While microwave heating of moist materials has long been state of the art, radio wave heating is less common but has the advantage of high penetration depth (in the range of meters) into materials of any moisture content. Both methods can achieve high overall efficiencies (>80%) for the conversion and incorporation of electrical energy in the form of heat.

Research needs

» A broad portfolio of catalysts, methods and process concepts for the use of electrical energy must be developed to meet the broad product range of chemical value creation.

» The new processes require catalysts and/or the combination of different types of catalysts that efficiently use the comparatively expensive electrical energy to synthesize high-cost chemicals.

1.5 Biotechnological and photo-electrochemical processes

Vision

» Solar power generation and water electrolysis can be efficiently combined in one component.

» In the fields of biophotolysis and biophotovolta-ics, the natural photosynthesis of cyanobacteria is used to directly produce H2 with efficiencies up to 20%.

» The CO_2 footprint, resource requirements and costs of biotechnological processes are minimized.

» Hydrogen can be economically produced in one step directly from water and only by means of solar energy.

The importance of disruptive technologies in the dynamic field of energy and hydrogen technology has been particularly evident in the past with innovations in biotechnology and photovoltaics, which have led to a rapid expansion of biogas capacity and solar power production.

Biotechnological use of solar energy

Efficient biocatalytic processes for the production of hydrogen from water are based on the natural photosynthetic apparatus of cyanobacteria. Their maximum theoretical efficiency is about 20 % for the conversion of light energy into H_2 directly at photosystem II, bypassing biomass production. Such processes fall under industrial (white) biotechnology, hence the term "white hydrogen".

Hydrogen is formed either by hydrogenases that release electrons directly from the primary reaction of photosynthesis (biophotolysis), or indirectly, e.g. at a cathode after anodic oxidation of components of the primary photosynthetic electron transport chain (biophotovoltaics). The biotechnological use of solar energy for direct hydrogen formation aims at decentralized production processes with an annual productivity of 0.5 - 1 ton H_2 per plant, a minimum required logistics for storage/transport and an on-site use of the hydrogen, e.g. via fuel cells for heat or electricity.

The turnover numbers and maximum efficiencies of the enzyme cascades involved allow maximization of the space-time yield for hydrogen at biocatalyst (biomass) densities of about 20 g dry weight per liter reaction volume. To avoid light limitations, the surface area must be maximized while maintaining high catalyst concentrations, e.g., in microcapillaries with immobilized biocatalysts in the form of biofilms on the inner capillary surface. This additionally enables continuous reaction control.

The product of biophotolysis is a mixture of oxygen and hydrogen. A fast and efficient separation of oxygen is essential, since hydrogenases are sensitive to oxygen and an O_2/H_2 mixture represents a safety risk. The need for closed redox balances with continuous hydrogen formation therefore requires physical separation processes of H_2 and O_2 in re-
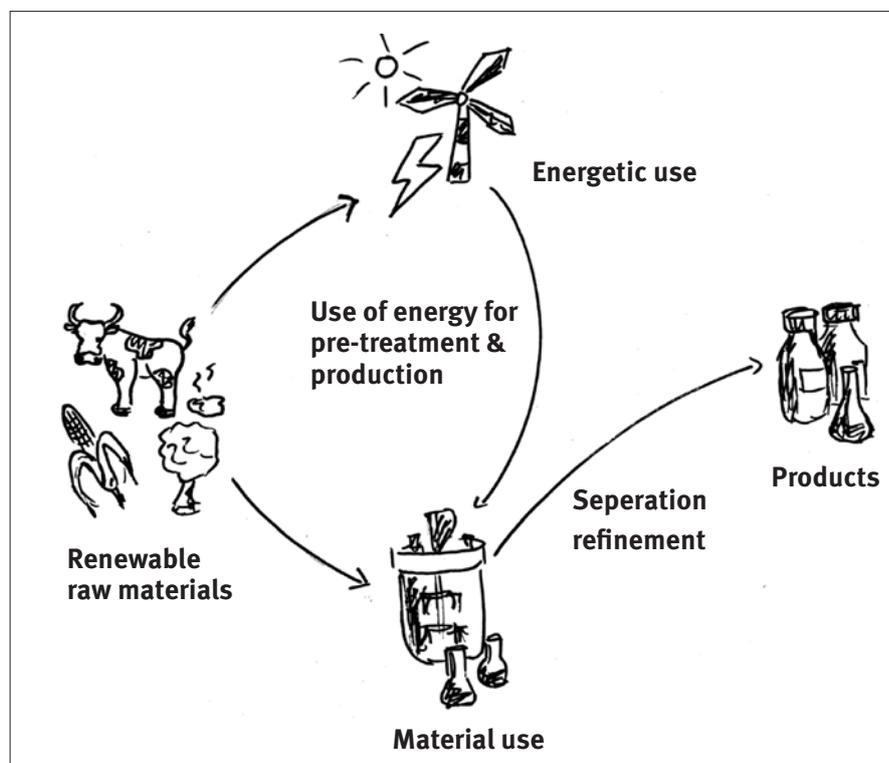

Figure 7: Simplified principle sketch of the electrobiorefinery concept: synergies can be generated by linking microbial and electrochemical material conversion in different stages. (© DECHEMA/F. Enzmann)

Energetic use

Use of energy for pre-treatment & production

Products

Seperation refinement

Renewable raw materials

Material use

action equilibrium. The oxyhydrogen problem is avoided in biophotovoltaics by the spatial separation of H_2 formation (cathode) and O_2 formation (at the biocatalyst, the cyanobacterial cell). An advantage of biophotovoltaics is the possibility of hydrogen formation at night from cellular storage materials (with correspondingly lower efficiency). Upcoming challenges are to increase the stability of the biocatalysts, to increase the efficiency towards the maximum upper limit of about 20 % with continuous reaction control (stabilization of the H_2 formation rate), to scale up the process while maintaining the advantages of large surface-to-volume ratios (microreaction technology), to couple H_2 storage for as short a time as possible with local utilization, and to conduct the reaction under real outdoor conditions.

Photoelectrochemical utilization of solar energy

The conversion of solar energy into electricity by means of photovoltaics is state of the art. It offers further possibilities for storage in chemical energy carriers: In addition to the electrocatalytic conversion of starting materials described in the previous chapter, sunlight can also be used directly to synthesize substances with higher energy content. This can happen in photocatalytic and photoelectrochemical processes via photoexcitation of charge carriers in semiconductors or molecular photoabsorbers, or by using sunlight to generate high temperatures (solar thermal energy). In both reaction modes, the goal is to enable reactions that are endergonic at ambient conditions, because only then will the energy from the sunlight be stored in the products generated. Such "uphill" reactions are often referred to as "artificial photosynthesis". Important examples are the splitting of water into green hydrogen and oxygen, and hydrogenation or cracking reactions of carbon dioxide. In the latter case, the most important greenhouse gas in terms of quantity can be recycled into chemical production. Recent studies are also looking at the direct reduction of atmospheric nitrogen to ammonia with the aim of replacing the energy- and raw material-intensive Haber-Bosch process with a decentralized and sustainable alternative. In solar thermochemical processes, concentrated solar energy is used to realize a redox cycle via non-stoichiometric oxides (CeO_2, Er_2O_3, $LaAlO_{3-\delta}$). Partial reduction of the metal oxide under inert gas and oxidation in the presence of H_2O and CO_2 are the key steps to generate syngas.

At first glance, it is obvious that an industrial implementation of photocatalytic, photoelectrochemical and solar thermal processes would require fundamental restructuring in the production chain. For example, light input

to large areas - or to small areas in concentrated form - would have to be made possible. Furthermore, photon-driven reactions are often carried out in the liquid phase.

So far, none of the above reaction routes have been able to obtain yields that are industrially relevant. This is one of the greatest challenges in this field of research. In order to achieve significant improvements, various hurdles have to be overcome. These include, for example, the generation and handling of large current densities in photoelectrochemistry and the efficient separation of charge carriers in particle-based photocatalyst systems. In addition, the widest possible wavelength range of sunlight must be absorbed to generate sufficient charge carriers. Improving charge separation is particularly challenging in particle-based photocatalysis because no external electric field can be applied for separation. Here, research concepts such as faceting of semiconductor particles and selective attachment of co-catalysts need to be explored more. Tailored semiconductor-catalyst composites or devices designed based on a fundamental understanding of interfacial energetics can lead to significantly improved charge carrier separation and thus higher solar-to-product efficiencies. In addition to activity, the stability of semiconductor-catalyst composite systems and the availability of the elements used are of particular importance for subsequent large-scale use in chemical energy conversion and storage.

The development of novel metal oxides with the aim of improved solar thermal synthesis gas generation under steady-state energy supply remains a research focus. However, their efficiency/stability under intermittent energy supply and integration with downstream processes have not yet been evaluated. Therefore, future research needs to address the fundamental understanding of the parameters that enable dynamic integration of thermal H_2O-CO_2-co-reduction with downstream syngas conversion processes and achieve improvement in the efficiency and lifetime of the materials.

Research needs

» Scalable biophotolysis and biophotovoltaic processes need to be developed for decentralized production.

» In continuous, decentralized processes, H_2 production must be stabilized and light-to-H_2 efficiency increased to 10%.

» Research approaches to increase solar-to-product efficiencies in photocatalysis & photoelectrochemistry through improved catalyst-semiconductor composites should be intensively pursued.

» Research for stable and energetically as well as structurally optimized bonding of efficient electrocatalysts to semiconductor photoabsorbers has to be intensified.

» Research into the scalability of the materials and production steps used and the reduction or substitution of precious metal content must be driven forward.

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2 From fossil raw materials to a cycle of carbon resources

The guidelines of sustainable development require a transformation of today's linear chemical industry with the aim of closed carbon cycles. In this context, renewable energy can be used as an energy/heating source and to provide chemical redox equivalents, e.g. in the form of hydrogen or electrons. Catalysts are essential to enable selective chemo-, bio-, or even electrocatalytic reactions in the face of materially varying resources. As carbon sources, fossil feedstocks must be used as carbon efficiently as possible in a transition phase and consistently replaced by renewable carbon sources such as CO_2 and biomass, as well as recycling streams, e.g. in the form of plastics-based recycling streams. Catalysts make it possible to selectively convert raw materials that are highly diverse in functionality and reactivity, and to develop efficient value chains that are geared to the needs of a circular economy. Catalysts are also the key element to realize energy-efficient carbon cycles. In particular, chemical energy storage molecules that allow transport and storage of renewable energy will gain importance as intermediates in chemical value chains and strengthen the coupling of the chemical and energy sectors. In the following, Chapter 2 addresses the requirements for catalysts and catalytic processes for the production of basic chemicals in line with the guiding principle of the circular economy and based on the diversification of the raw material base presented.

2.1 The guiding principle of catalysis in the context of the circular economy

Today, the value chains of the chemical industry are linear; starting from predominantly fossil raw materials, products are produced, used and then "disposed of" via a limited number of key intermediates. In the past, sustainability was mostly limited to concerns about availability, safety aspects in handling and direct impact on the environment (emission, immision, toxicity, etc.). Only the realization that this linearity also leads to an accumulation of greenhouse gases and thus changes the climate and general living conditions has changed the view on linear value chains. Circular value chains and an energy-efficient circular economy, especially related to carbon, are therefore the focus of attention.

The catalytic processes central to all chemical processes are the key to the gradual transformation to a circular economy. It requires nothing less than the consistent transformation of existing value chains (Agenda 2030 UN[3]). In addition to an often unmanageable set of specific technical problems in this transformation, the central question is the size of the cycles. At the extremes, circularity can be seen as recycling within a product group (e.g., polymers) or as a carbon cycle (from functional molecule to CO_2 and back). However, because strategies must consider not only technical but also systemic and social aspects, for catalysis, developing alternative routes to chemical recyclables that minimize CO_2 accu-

mulation is a categorical imperative. It is equally a categorical imperative to obtain the energy required in these conversions from renewable sources.

Topics of high relevance are the use of renewable or reusable raw materials in the form of biomass, used chemical recyclables (e.g. plastics) and CO_2. Of particular importance is the polymer sector, which accounts for about 90% of the total production volume of all chemicals (carbon-based). In contrast to specialty chemicals, polymers make it to the end user and the majority of them (worldwide) are still landfilled or dispersed in an uncontrolled manner. New processes that make polymers usable as raw materials at the end of their life cycle can address this challenge in terms of circularity.

Given the magnitude of this transformation of the economy and the highly diversified feedstock base, changes must be compatible, i.e., chemical value chains should be largely maintained and only gradually transformed. Therefore, new catalytic processes are essential to continue providing established key intermediates ("drop-in" processes) with low CO_2 footprints.

While "drop-in processes" enable a gradual transition to a new economy, new catalytic processes are essential to enable carbon and energy efficient access to new intermediates. The changing and diversified feedstock base, e.g. CO_2 or biomass, also requires flexibility in terms of joint processing of different feedstock sources. Sustainable and both technically and economically viable processes require catalysts capable of enabling these conversions selectively, as well as atom- and energy-efficiently and, if necessary, even with fluctuating renewable energy supply.

Altogether, this means that a construction kit of catalytic processes must be developed and gradually used in production. Since at the same time the energy input for the chemical processes is to be obtained from renewable energy, the transition period will see a variety of forms of energy input with at the same time significant diversification of the input materials. It should be emphasized here that this transition will extend over a period of at least 30-50 years.

The fossil carbon sources currently used are mainly coal, oil and natural gas, and to an increasing extent biogenic raw material. All raw materials are globally available, but

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3   https://unric.org/de/17ziele

local deposits lead to strong price differences and thus to preferential use (e.g.: China: coal, USA: shale gas). Fossil carbon resources are available in sufficient quantities for several 100 years, but their unlimited use with established technologies will not lead to a reduction in greenhouse gas emissions.

It is important to link sectors of the chemical industry and the energy industry in the conception of a circular economy ("sector coupling"), i.e. to optimize them in a joint, overarching approach. The storage of energy generated from renewable sources in chemical compounds requires the coupling of industry segments in terms of energy and materials. This creates new potentials, but potentially also temporary bottlenecks. Examples include the low spatial density of energy production and the temporal fluctuation of energy production, as well as the alternative dynamics of biogenic feedstock availability compared to fossil carbon sources.

Transition technologies that can be implemented quickly are of particular importance for the rapid reduction of climate-relevant emissions. These must have a significant advantage over existing technologies in terms of energy efficiency and specific CO_2 emissions. Such transitional technologies are not yet completely climate-neutral and will be partially based on fossil raw materials. The approach is particularly interesting if existing infrastructure can be used. Examples of such technologies are the production and use of hydrogen based on methane pyrolysis with carbon capture (turquoise hydrogen), first-generation bioethanol, or methods for sorption of CO_2 from exhaust gases (carbon capture and sequestration). Ideally, the latter approach already converts a significant amount of CO_2 to chemical intermediates (CCU, "carbon capture and use").

2.2 Catalysts for carbon efficient use of fossil resources

Vision

» Fossil raw materials are used carbon efficiently in transition technologies using high-performance catalysts and catalytic processes.

» Catalytic conversions take place using green hydrogen and renewable energy.

» Catalysts enable the gradual transformation of petrochemical and refinery processes through (1) increasing use of renewable carbon sources in established processes and (2) the use of alternative conversion processes of renewable feedstocks in refining and petrochemicals.

» Endothermic and exothermic catalytic processes are coupled with the goal of high energy efficiency.

Crude oil (and to a lesser extent natural gas) have been the preferred feedstocks in the petrochemical and petroleum industries to synthesize carbonaceous valuable materials. Facilities for the conversion of these feedstocks are available worldwide, as are highly efficient logistics and distribution networks. Refinery processing is largely optimized in terms of energy and material utilization of crude oil. The goal of a typical complex refinery is to distribute the size of carbonaceous molecules across a given product spectrum and to set an H/C ratio of about 2. This goal is achieved by redistributing hydrogen between molecules ("hydrogen addition") and by eliminating carbon ("carbon rejection"). The carbon eliminated from the crude oil is burned and the heat is used. Refineries have the potential to become an important part of the transformation through their versatile equipment. Three aspects are essential here:

1 no fossil energy is used for the conversion processes (replacement by electrification based on renewable energy),

2 "green hydrogen" is used to increase the H/C ratio and.

3 Carbon is preserved to the maximum.

As moderate as these changes sound, they require a radical redesign of the refinery's catalytic processes. For example, the elimination of carbon (and its oxidation) in processes such as fluid catalytic cracking must be replaced by the addition of hydrogen (hydrocracking with adapted catalysts). The potential to reduce the specific CO_2 emissions of the products is significant.

Refineries can also become central nodes in future carbon cycles in conjunction with green hydrogen. The possibility of using gradually recycled carbon streams is in principle limited only by the (energetic) costs of transporting the raw materials. In the case of chemical recyclables such as polyolefins, their chemical composition with an H/C ratio of 2 is ideal for the entire product spectrum. In the case of biogenic materials (sewage sludge, biomass), which have to be processed by pyrolysis or hydrothermal processes, the carbon introduced is conceptually used as a storage for green hydrogen, and electrical energy is stored in chemical bonds via the detour of water electrolysis.

However, it is conceivable that the classic coupling of the petrochemical industry to the refining industry via naphtha as an intermediate step will weaken and/or be replaced by direct processing of ethane and propane (from shale gas). In contrast, direct low-cost production of small olefins and high-value aromatics cuts may play an increasingly important role.

As a transitional technology and depending on the location, it is also possible to convert CO_2 directly to hydrocarbons (e.g. Fischer-Tropsch process) up to a spectrum of drop-in products. However, it is worth remembering the enormous scale of the transition to a CO_2-neutral economy: replacing 10% of the amount of fossil energy consumed annually is equivalent to about 75,000 wind turbines, or more than twice the amount now installed. Since the total replacement of fossil energy would require a wind farm the size of Baden-Württemberg, it is predictable that Germany will import carbon-based energy sources, and refineries, while changing, will continue to be a central part of the infrastructure.

The future challenges for the oil-processing industry therefore lie in the direct use of sustainably produced hydrogen, the gradually growing share of new carbon sources such as biomass and plastic waste, and the declining use of natural gas and crude oil. Depending on the changing raw material sources, today's common processes will have to be rescaled and at least partially redeveloped.

Fluid catalytic cracking, FCC, now central to many refineries, is an important element of such considerations. As it stands, the energy to crack hydrocarbons is derived from the combustion of a portion of the feedstock in the regenerator. To reduce CO_2 emitted in the process, for example, electric resistance heating would have to be used and captured carbon would have to be converted with water and oxygen to synthesis gas. This synthesis gas can in turn be used in alcohol or Fischer-Tropsch synthesis. In such a concept, pyrolysis oils from biogenic sources or polymer waste can gradually replace the conventionally used vacuum gas oil. Especially for more oxygenated feedstocks, stronger reducing atmospheres in the riser reactor can also be considered to reduce carbon deposition. In the FCC, (zeolite) catalysts with minimal coking tendency are required accordingly, e.g. through hierarchical pore systems and adapted acid centers or even integrated redox activity.

A second major area is hydrotreating[4]. If sulfur and nitrogen as heteroatoms determine the activity and selectivity of catalysts today, biogenic carbon sources increasingly provide oxygen-containing molecules (e.g., from hydrothermal processes or mild pyrolyses). Sulfidic catalysts of high stabil-

Figure 8: Illustration of a gradual transition to new raw materials.
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4 Hydrotreating includes a removal of sulfur, nitrogen, and oxygen by hydrogenative cracking.

ity even at low sulfur contents in the feed are required for this purpose, as are mono- and bimetallic catalysts of high performance in hydro-deoxygenation with at the same time a low tendency to C-C bond cleavages. Catalytic reforming of hydrocarbon fractions (gasoline cut) continues to be an important source of aromatics and for isomerization. Smaller processes, such as oligomerization of alkenes, alkylation and hydro-isomerization of alkanes remain important in future refineries.

Research needs

» Catalysts and catalytic processes for new hydrocracking technologies to maximize renewable hydrogen use and minimize carbon loss need to be developed.

» Hydrotreating[4] catalysts should be optimized to achieve high selectivity and activity for C-O, C-N, or C-S bond cleavages even at low temperatures, while maintaining a low tendency for C-C bond cleavage and coking.

» Zeolites and other solid acid catalysts are to be optimized for modified FCC processes with flexible feedstocks at low coking (carbon formation on the catalyst).

2.3 C_1 compounds as raw materials for basic chemicals

Vision

» Selective catalytic CO_2 hydrogenation to C_{1+} products of the different reduction stages corresponding to CO, formic acid, formaldehyde, methanol and methane is possible.

» C_1 Energy storage molecules (hydrogen storage) are also important intermediates of chemical value chains, thus linking the energy and chemical sectors.

» Direct chemo-, bio- or electrocatalytic activation of methane to C_1 compounds of higher oxidation state or C_{2+} products is possible.

» Value chains can be flexibly served by different C_1 sources.

2.3.1 Methane as a raw material

Methane, especially as a chemical energy carrier from the hydrogenation of CO/CO_2 or also in the form of biomethane, will play an important role for the import of green energy. The already established natural gas network can be used directly for green methane. As a carbon source of chemical value chains, methane will remain an important building block for syngas production. In addition, routes such as mixed or dry reforming, which allow CO_2 injection, will gain importance. Such processes allow a materially highly efficient conversion of CO_2, but are limited in quantity. Especially in the case of mixed or dry reforming, the electrification of the reactors can make a significant contribution to reducing CO emissions.

Catalytic partial oxidation also has high potential in the area of CO_2 emission reduction, but still requires optimization. The direct chemocatalytic oxidative conversions of methane to methanol or formaldehyde remain "dream reactions" and require fundamental theoretical and experimental investigations. Electrocatalytic methane activation processes should also be intensively considered. Chemocatalytic methane activation by oxidative coupling to ethylene and ethane is promising, and integrated reaction engineering approaches are essential. The use of data-driven processes has proven to be an important tool in this regard.

The one-step (oxidative or non-oxidative) production of benzene and other aromatic molecules from methane has high economic hurdles, as does oxidative coupling. Key development goals are active and stable catalysts in combination with coordinated energy and material process integration.

2.3.2 CO and CO_2 as raw materials for basic chemicals

Synthesis gas chemistry is firmly established as a conversion technology in the chemical and energy industries. Many conversion technologies are largely mature and belong to the standard processes. The high specific process efficiency leads to low specific emissions coupled with high product yields and selectivities. However, classical oxo processes (hydroformylation, acetic acid production) are subject to increasing cost pressure. New approaches of carboxylations start here, as both the low raw material price of carbon dioxide and its easy manageability mean a technically low barrier to entry. High-volume chemicals that can be produced via carboxylation reactions make carbon capture & utilization (CCU) attractive. In addition to the established carboxylation of aromatic substrates, the carboxylation of olefins is a major challenge. Progress in the production of Na-acrylate with homogeneous catalysis demonstrates the potential. New, high-performance catalysts are needed for a "carboxylation platform" for other important chemical intermediates.

Carbonylations also hold great potential, e.g. for the selective carbonylation of alkenes, aromatics and oxygenates such as methanol, DME and methyl acetate. Especially for carbonylation reactions, the energy efficiency of the production across all steps plays an important role. Levers for low specific energy input in the process are low pressures, the use of gas phase carbonylation technologies (example BP process DME to AcOH, new approaches in the field of gas phase hydroformylation by SILP (supported ionic liquid phase technology) and transition metal phosphides) and low energy input in product separation. New fields of development in hydroformylation lie in the expansion of the portfolio of technologies for hydroformylation with mixtures of CO /H2 (in the sense of a CCU), mixtures of olefins and the hydroformylation of "new" products from the fields of fine chemicals and active ingredients (see Chapter 4).

The catalytic direct conversion of synthesis gas to oxygenates and olefins, in particular also higher alcohols (C_3 to C_8) and olefins (C_2 to C_4), also re-
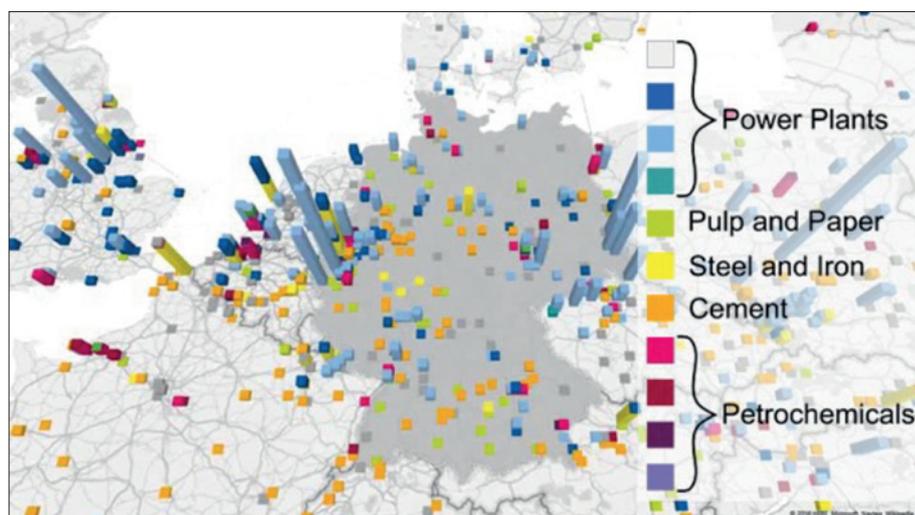

Figure 9: CO_2 emissions of different sectors[5]

quires significant developments with regard to selective, active and stable catalysts. CO /H_2 as well as mixed feed streams CO/CO_2 /H_2 also need to be considered.

Synthesis gas fermentation as a biocatalytic conversion of synthesis gas-rich waste gas streams or product streams from CO_2 co-electrolysis is promising. In particular, energy-efficient catalytic utilization of waste gases to produce high-value products or chemical energy carriers offers a high incentive for new developments.

Research needs

» New approaches in homogeneous catalysis are being pursued, with a focus on new lead structures in carboxylation chemistry.

» New approaches to reaction engineering and catalysis in gas-phase and liquid-phase low-pressure carbonylation are needed.

» The „hydroformylation" platform technology is being expanded to address new challenging synthons through new, readily accessible ligand systems.

» New approaches in the field of direct conversion of synthesis gas to higher alcohols and small olefins are consistently pursued.

» The biocatalysis platform for „synthesis gas fermentation" is to be systematically expanded.

» Efforts are being made to establish new routes to small molecules with function as energy carriers using new efficient technologies based on homogeneous and heterogeneous catalysis.

2.3.3 Methanol and DME as C_1 intermediates of chemical value chains

Methanol and dimethyl ether have immense value for sustainable and circular approaches due to the currently available technologies for their production and their excellent integration possibilities in value chains in the chemical and energy industries. In particular, the ability to convert CO_2 to methanol and DME via a range of established technologies lowers the technological barrier to their production and increases their potential availability. Both methanol and DME are readily transportable and storable, making them excellent storage media for periodic amounts of energy (see Chapter 1). Both methanol and DME are converted to olefins, aromatics, and alkanes (fuels) by acidic and shape-selective catalysts (zeolites). The resulting products are relevant to both the chemical and refining industries. Advantages over Fischer-Tropsch (FT) technology are the smaller plant size required to achieve economic viability and the high flexibility for selective product manufacture. FT plants usually require very large plants and often the coupling with another processing step (hydrocracker, reformer, platformer). The highly selective methanol and DME downstream processes, on the other hand, are potentially economical even at small and medium scales and allow integration adapted to the required size. Decentralized operation is also conceivable. Processes for the direct conversion of synthesis gas to olefins are subject to similar boundary conditions as the FT process. The known process concepts are hardly flexible with regard to the product spectrum and the necessary reintegration of the CO_2 produced.

Other catalytic functionalizations starting from methanol and DME to halogen-containing feedstocks such as methyl chloride for niche applications, methylamine, methanethiol and methyl formate are also possible.

Research needs

» The development and molecular understanding of catalysts and catalytic processes for conversion of MeOH and DME to olefins, aromatics and alkanes are being advanced.

» Sustainable concepts for the chemical upgrading of methanol and DME are being developed.

2.4 Biomass residue streams as raw material

Vision

» Real biomass residue streams can be converted in catalytic processes.

» Stable catalyst systems for reactions in aqueous media are available.

» The role of solvent in heterogeneously catalyzed liquid-phase reactions is understood.

» Biomass serves as a functional carbon source that is integrated into existing and new value chains through selective catalytic transformations.

» The molecular basis of selective catalytic deoxygenation of multifunctional biomass intermediates is understood.

» Catalysts for selective chemo- and electrocatalytic partial oxidation of biomass-based intermediates are available.

» Catalysts for selective catalytic conversion of biomass-based intermediates to nitrogen-containing compounds have been established.

Biomass, as a renewable carbon source, offers great structural diversity for access to tailored monomers and the potential of closed CO_2 cycles. By using biogenic residue streams, competition with food production can be avoided. However, regional and seasonal fluctuations in biomass production must be taken into account in the supply of raw materials for chemical processes, as must a limited radius of economic raw material transport.

In biomass, CO_2 from the atmosphere is already bound and chemically partially reduced, converted into plant material by photosynthesis. The main scientific and technical challenges are the high levels of oxygen, nitrogen and, to a lesser extent, sulfur. The significantly higher degree of oxidation requires the introduction of H_2 at an early stage of conversion and the avoidance of high temperatures to minimize condensation processes. Pyrolysis is an established process to reduce the water content in biomass streams and to develop biomass as a feedstock stream (bio-oils). Further processing via hydrotreating (hydrodeoxygenation) to hydrocarbon or oxygenate mixtures has been extensively investigated over the last decade, with a need for research particularly in the area of highly active sulfidic catalysts (e.g. NiW sulfides). Alternatively, bio-oils are converted to synthesis gas (e.g. bioliq®) and can then be integrated into value chains with the aid of (conventional) synthesis gas catalysis.

Efficient technologies for the extraction of defined raw material fractions from lignocellulose are the prerequisite for the development of new value chains starting from biomass.

Starting from single fractions (lignin, cellulose, hemicellulose), biotechnological or chemocatalytic process-

Figure 10: Biorefineries will be a fundamental part of a future chemical circular economy.
(© Adobe Stock / Andrei Merkulov)

es can be used to selectively obtain key intermediates. Particularly important is the hydrolysis and fermentation of cellulose streams to bioethanol (dehydrogenation to bio-ethene). Commercially, biotechnological processes are used to produce selected acids (fatty acids, amino acids as well as monomers such as lactic, succinic or itaconic acid) as well as diols (e.g. 1,3-propanediol, 2,3-butanediol). Development potentials lie especially in continuous processes also with integrated product separation, e.g. to address challenges of product inhibition. In addition, so-called metabolic funneling, i.e. the possibility of selectively producing individual target products from a wide variety of carbon sources using biotechnological processes, is important for a diversified raw material base.

Cellulose and hemicellulose can be chemocatalytically converted to the polyols sorbitol and xylitol. By means of selective hydrodeoxygenation, ethylene and propylene glycol or by means of dehydration, e.g. isosorbide, are accessible as monomers. Selective hydrogenations and hydrodeoxygenations, such as those required to convert 5-hydroxymethylfurfural, furfural or sorbitol/xylitol to 1,2- or 1,5-/1,6-diols, remain challenging. Selective hydrogenation of carboxylic acids also requires the development of new powerful catalysts that allow selective access to aldehydes and alcohols even under mild reaction conditions. Oxidations of cellulose and hemicellulose make formic acid accessible.

A wide range of hydroxycarboxylic acids, their dehydrated derivatives and of dicarboxylic acids can be prepared by combining chemocatalytic and biocatalytic processes. These compounds represent promising monomers. Selective reduction opens up access to diols, for example. The commonly used acrylic acid is preferably produced from 3-hydroxypropionic acid by dehydration, from glycerol by dehydration to acrolein and subsequent selective oxidation, or from lactic acid by dehydration over zeolites exchanged with alkali cations. Selective oxidation of key intermediates such as sugars, glycerol, or 5-hydroxymethylfurfural also requires powerful catalysts for selective conversions to aldehydes and acids at mild conditions in the presence of many similar functional groups. In addition to oxygen functions, efficient catalytic conversions to nitrogen-containing products are essential, for example to diamines and monomers such as acrylonitrile or pyrrolidones.

Also of high relevance is catalytic access to aromatics from lignocellulose or pure lignin via pyrolytic and hydrogenolytic routes. Substituted phenols are accessible

by mild acidic or basic hydrolysis. Catalysts that allow sufficient selectivity to selected products are an important research goal.

The main challenges of biomass as a raw material are selective transformation, processing in liquid-phase processes due to limited thermal stability and high polarity, and the often high energy requirements of separation processes due to highly polar products and aqueous, and in the case of biotechnological processes also mineral-containing, material streams. Technologically, it is necessary to

1   reduce the polarity of products early in the value chain or
2   develop catalytic processes in the sense of reactive separation processes that address these challenges or
3   establish suitable processes for coupling with aqueous, possibly saline, material flows.

For the latter aspect, electrochemical processes represent an interesting approach which, on the one hand, allows aqueous material streams containing electrolytes to be processed directly and, on the other hand, allows renewable energy to be coupled directly into chemical value chains. By coupling suitable anodic and cathodic reactions, so-called 200% reactions become possible, which deliver economically interesting target products with high efficiency at both electrodes.

Over a decade of worldwide research into the conversion of biogenic feedstocks to chemicals and energy sources has led to the development of an impressive variety of reaction routes and catalysts, documented in well over 2000 review articles. The major challenge lies in the selective conversion to target molecules from a mixture of starting materials. Understanding the complexity, entanglement of (kinetics of) conversion, and stability of catalysts are the major challenges. Data science and artificial intelligence are important tools for conceptual advancement

Research needs

» The development of new selective catalysts and processes for the deoxygenation of biomass components is consistently pursued.

» The development of catalysts for the selective hydrogenation and oxidation of platform chemicals under mild conditions, in particular also in protic solvent systems, is to be intensified.

» In reactive catalytic processes, catalytic conversion and mass separation are to be integrated.

» Analytical and theoretical methods are established for understanding molecular processes at catalyst surfaces in liquid phase and electrochemical processes.

» One research focus is on the close interlinking and, if necessary, integration of biotechnological, chemocatalytic and, if applicable, electrocatalytic processes.

» Catalysts for selective electrocatalytic conversions, preferably in the form of combined anodic and cathodic reactions in the sense of 200% reactions, are to be developed.

» An early assessment of the economic and ecological potential of new catalytic conversions is carried out.

2.5 Plastic waste as raw materials

Vision

» Catalytic recycling processes for plastics enable even mixed and contaminated plastic fractions to be selectively converted into defined chemical building blocks while preserving the chemical structure and functionality as far as possible.

» Pyrolysis processes are technically simple, universal and raw material-tolerant processes. Future pyrolysis processes will also allow maximum preservation of the chemical functionality of the feedstocks, e.g. in the form of catalytic pyrolysis.

» Catalysts for the further processing of pyrolysis oils make it possible to introduce pyrolysis oils as raw materials into value chains.

» New catalytic processes for chemical recycling make it possible to recover the original monomers or alternative products with the highest possible added value from plastics (open-loop recycling).

Around 70 years ago, plastics became an industrial mass product. Plastic products play a central role in many areas of life and industrial sectors. Currently, a steadily growing range of synthetic polymers is being developed and produced to meet the diverse demands of industry and consumers. The finite resource for these resistant materials is predominantly fossil raw materials. Only recently have a few bio-based alternatives been industrially implemented. However, the steadily increasing production and use of synthetic polymers remains unsustainable as long as efficient recycling processes for these materials are lacking. To date, only 9% of the 8.3 billion tons of synthetic polymers produced since 1950 have been recycled.[6] The result is an enormous growth of plastic waste as well as its accumulation in the environment. For a sustainable solution to this current and highly relevant problem, novel catalysts and powerful catalytic processes are essential to establish polymers as a sustainable raw material source of a resource-efficient circular economy including renewable energy and further carbon sources.

The challenges for establishing such a circular economy for polymer waste lie, on the one hand, in the (partial) replacement of petrochemical feedstocks and, on the

6 R. Geyer, J. R. Jambeck, K. L. Law, *Sci. Adv.* **2017**, 3, e1700782.

other hand, in the true closed-loop management of carbon-containing (waste) material streams with minimal loss of carbon-containing building blocks. Key to a successful conversion are the minimal use of energy and chemical energy equivalents in the conversion of waste streams available to the chemical industry for reprocessing, and the minimal emission of greenhouse-relevant gases.

Pyrolysis technologies are of central importance in the recycling of plastic waste. These are particularly suitable for converting plastic waste into highly aliphatic or aromatic pyrolysates. Purification of such pyrolysates and removal of heteroatoms are challenging. New approaches to catalytic hydropyrolysis are still in the conceptual phase, but have great potential to reduce the number of necessary conversion steps and technologies.

Especially in the field of heteroatom-containing polymers, which are usually produced by polycondensation from heteroatom-containing monomers, the introduction of the heteroatoms into the respective monomer structures is very energy-intensive. Therefore, future concepts of chemical recycling must aim at preserving the respective functional groups in the molecule during depolymerization. Defined plastic fractions are a prerequisite.

Mixed and highly contaminated waste streams, for example from the field of composite materials or highly heterogeneous waste such as light shredder fractions and waste from the field of construction material recycling, present a different challenge. Such waste streams are usually not easy to process, since they vary greatly in terms of both the type and composition of their individual components and contain high proportions of inorganic components. Pyrolysates from such waste streams can vary greatly in composition depending on the source and place high demands on processing.

Research needs

» Robust catalysts for catalytic pyrolysis of mixed plastic waste fractions will be developed.

» Research will advance the development of selective catalysts for catalytic pyrolysis to defined product mixtures with maximum retention of chemical functionality.

» Efforts are being made to establish catalysts and catalytic processes for the purification of pyrolysis oil. Here, a particular focus is on the energy-efficient removal of interfering heteroatoms. In detail, the respective pyrolysis oil streams differ in composition depending on the feedstocks and production processes. The challenge for catalysis is to provide adapted solutions for the respective material streams.

» Catalysts and catalytic processes are being developed for the cleavage of heteroatom-containing polymers while retaining the heteroatoms and monomer functionality. The particular focus here is on high selectivity in the cleavage process with the lowest possible specific energy input.

» Concepts for catalysts and catalytic transformations for chemical recycling of different plastic fractions to monomers or higher value products will be advanced, according to the concept of open-loop recycling.

Figure 11: Efficient processes for recycling even mixed plastic fractions are of great importance for a viable chemical circular economy. (© Pixabay / pasja1000)

2.6 Alternative approaches to key intermediates

Vision

» Key intermediates of chemical value chains are accessible from different raw materials depending on temporal and spatial raw material and energy availability.

» Selective catalysts for C-C bond linkage starting from various sustainable C_1 intermediates are available.

» Experimental and theoretical methods to elucidate surface molecular reactions form the basis for understanding-based catalyst development.

Alternative accesses to basic chemicals may gain importance in the future due to a better specific CO_2 footprint and high energy efficiency. Overall, such new processes are very difficult to place in a common context because, first, the feedstock base is diverse and, second, the underlying chemical and catalytic conversion technologies are fundamentally different. A common feature of such alternative routes is that the linkage of one or more C-C single or double bonds usually plays a role.

The electrochemical (cathodic) CO_2 activation, which leads to small olefins and oxygenates such as methyl formate or oxalates, is again being discussed intensively in the context of the recycling of greenhouse gases under the direct use of electrical energy. The increase of the specific energy efficiency by coupling with a suitable oxidation reaction such as methane to methanol at the anode can lead to a so-called 200% cell.

Acetylene can lead to a revival of acetylene chemistry as a "green" alternative to conventional routes based on olefins in the context of the energy transition as a "green" feedstock via "e-fuel" methane and a coupling with renewable energy in the Hüls arc process or by partial oxidation and use of the coupled product synthesis gas in integrated refinery locations.

Synthesis gas fermentation to ethanol and the fermentation of methanol and ethanol to higher alcohols and acid derivatives can also gain importance as platform technologies in the context of energy-efficient processing of greenhouse gases without the need for costly purification. Since such technology platforms generally require point sources of appropriate size and off-gas composi-

tion, they should be evaluated as B2B solutions or in the context of sector coupling.

Catalysis for complex condensation reactions can also open up a technology platform. Catalytic condensation reactions can offer interesting competitive approaches to flexible feedstock-based chemical intermediates that can be produced with low CO_2 footprint in a highly energy-efficient manner vis-à-vis traditional petrochemical value chains. Examples of such approaches include the use of catalytic Guerbet technologies, such as the conversion of ethanol to 1-butanol in the gas phase, and the conversion of acetic acid and formaldehyde to acrylic acid over VPO catalysts.

Research needs

» Catalysts and catalytic processes for chemo-, bio- or electrochemical C-C bond linkages starting from different C_1/C_2 intermediates will be systematically developed.

» One research focus will be on the development of catalysts for the further processing of products/product mixtures from (synthesis gas) fermentation.

2.7 Sustainability assessment

Vision

» Development goals of catalysis and catalytic processes are prioritized based on sensitivity analysis.

» The potential of novel catalytic reaction pathways is considered at an early stage in terms of energy efficiency and sustainability.

» Catalyst and process are developed synergistically.

2.7.1 Exergy analysis for catalyst and process development

A current focus in process and catalyst development is energy-intensive chemical transformation reactions, which are necessary, for example, for the production of chemicals or synthetic fuels from carbon dioxide. Sustainable production of products with high energy content requires high exergetic efficiency, i.e. low losses compared to thermodynamically reversible transfor-

mation. Exergy analysis is an established methodology for evaluating energy systems. Here, exergy is the maximum work that can be produced by equilibrating a system with its surroundings. Exergy analyses calculate the exergy dissipation or conversion to anergy and thus define the rational efficiency in terms of Carnot's cycle, i.e. how close the conversions are to reversibility.

In catalyst and process development, exergy analysis can play an important role in a numerical analysis to: (I) make a choice between target products and reaction pathways; (II) evaluate the catalyst type (e.g., homogeneous, heterogeneous); and (III) determine the desired catalyst optimization objective (e.g., selectivity vs. conversion vs. residence time vs. catalyst stability). In this sense, it is a supportive method to model-based rational decisions that requires less effort than rigorous mathematical modelling. Exergy analysis is also applicable when little experimental data is available. It uses important reaction characteristics (stoichiometry, equilibrium calculation, or given selectivity/conversion from experimental data) along with thermodynamic data (enthalpy, entropy) and the specific energy requirements. Close cooperation between catalyst experts and process engineers is required to collect the data sets necessary to perform an exergy analysis. The exergy analysis is manageable in terms of calculation effort and can be used in scenario and sensitivity analyses in relation to the decisions to be made.

Exergy analysis can sometimes even identify bottlenecks in a process and help improve catalyst and process design. This is not always possible because I) sometimes an inefficiency in one conversion step can lead to an exergy dissipation in another step and thus it is not clear which step needs to be improved; II) steps are coupled via heat and mass integration. Many concepts and methods have been proposed for energy systems, including extended exergy analysis, to overcome such challenges. Coupling with process modelling methods (intermediate-fidelity models, e.g., idealized reactor modelling) is also possible. Furthermore, exergy analysis can be extended to include economic considerations in the sense of a techno-economic approach.
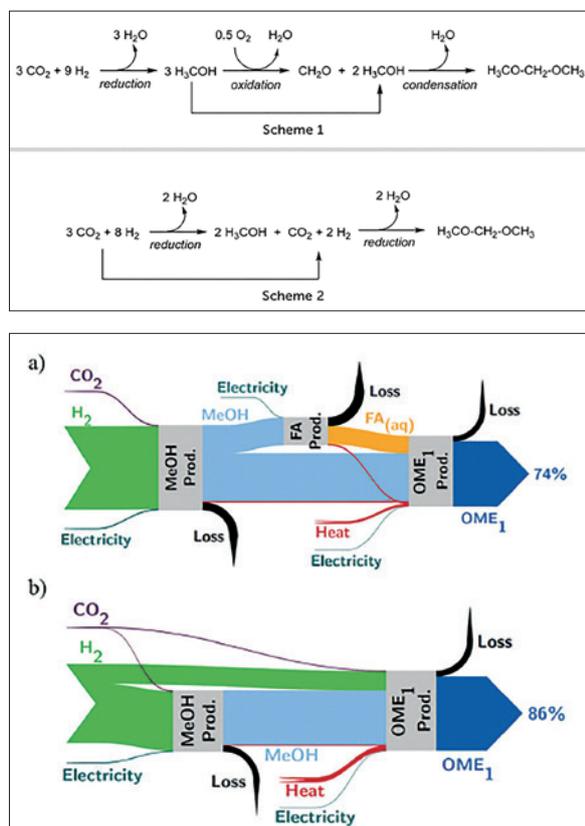

Figure 12: Comparison of two routes of OME1 (oxymethylene ethers) production (left) and the corresponding exergy fluxes (Sankey diagram, right). (© Deutz et al. 2018 (https://dx.doi.org/10.1039/c7ee01657c))

» Validation of exergy analysis methods for product and process selection and catalyst design will be performed.

» The focus will be on extending methods for coupling exergy analysis with other intermediate-fidelity models (e.g., idealized reactor modelling).

2.7.2 Life Cycle Assessment

Life Cycle Assessment (LCA) determines the potential environmental impacts of products and processes. Since catalyst development is often motivated by reducing energy demand and environmental impact, LCA is important for quantifying these benefits and potential trade-offs. The important feature of LCA is that it considers the entire life cycle from raw material extraction through production and use to recycling and end-of-life disposal. At the same time, the environmental impacts considered cover effects ranging from climate change to toxicity or noise. Life cycle assessment is used from product development to marketing and increasingly forms the basis for standards and regulations.

Life cycle assessment was standardized in the 1990s in ISO 14040/14044. The ISO standards provide a mature framework for environmental assessment and its documentation. Nevertheless, many methodological decisions remain open, so that LCA studies are often difficult to compare. Studies may even produce qualitatively different results, such as reporting positive or negative carbon footprints for the same chemical production process. Therefore, targeted LCA guidelines have been developed for the chemical sector and even for specific products and processes, e.g., carbon capture and utilization. The holistic perspective of LCA enables a balanced assessment of the sustainability of chemical processes, e.g., by identifying trade-offs between reduced climate change impacts and increased land use and potential toxicity impacts from agriculture for some bio-based chemicals. In this way, LCA steers technology development toward environmental hotspots.

The biggest practical challenge of LCA is the extensive data required: Heat and mass balances are required over the entire life cycle to account for all flows to and from the environment. This data is best available for mature technologies used in industry. LCA databases collect this information, but still cover only a small portion of the chemical industry with its wide variety of products and processes. Data on catalyst production and use tend to be the most proprietary and therefore least available. Methods have been developed to fill data gaps, but these increase the uncertainty of LCA results. The data required for LCA are particularly lacking in the early stages of development, when the potential to steer technology toward environmentally beneficial solutions is greatest. Therefore, LCA methods for emerging technologies are an important focus of current research. In catalysis, this lack of life-cycle data and knowledge is particularly severe for alternative feedstocks and energy sources. In this case, not only are the catalyst and corresponding processes under development and not yet known, but also the supply chain for the alternative feedstock. Recent efforts in LCA aim at establishing consistent scenarios for such background processes. For the end-of-life of novel catalytic structures and chemicals, information on the potential release, fate and impact in the environment and on human exposure is usually lacking.
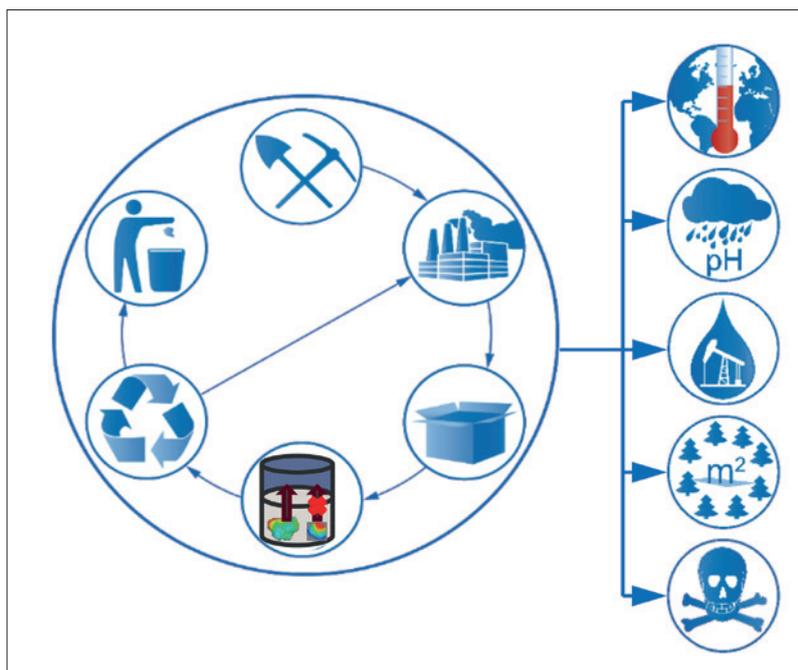
Figure 13: Life cycle assessment showing the life cycle from cradle to grave and the resulting environmental impacts from climate change to toxicity.

LCA is sometimes equated with sustainability. However, LCA focuses on environmental impacts and regular operations. Therefore, environmental risks and safety are not considered, nor are economic and social dimensions. Integrating all environmental, social, and economic impacts over the entire life cycle is the goal of Life Cycle Sustainability Assessment (LCSA), which is currently a very active area of research.

Research needs

» A development of LCA methods and tools for emerging chemical technologies that can leverage data generated during catalyst and process research, from high-throughput experiments to computational chemistry, should be pursued as a high priority.

» There is a need to develop methods for closing the feedback loop from LCA to catalysis and process research by linking environmental impacts to degrees of freedom in catalyst design.

» Further development of methods for rapid assessment of novel catalyst structures and chemical products with respect to human exposure and environmental release, fate, and effects must be pursued.

» Standardized workflows and decision support for sustainability assessment in catalyst and process development need to be established and addressed by integrating LCA with complementary approaches to consider risk, environmental, economic, and social impacts.

» Use of existing data: Methods will be developed that take into account the technology readiness level and available existing data.

» Numerical method development: Numerical optimization with embedded exergy analysis should become usable for rational decisions in process and catalyst development.

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3 Climate and environmental protection

Catalysis makes a significant contribution in processes to keep air, water and soil clean and to protect the environment. For the reduction of emissions from mobile and stationary combustion sources, it holds a firm place in technical applications. In the field of automotive exhaust gas cleaning, catalysts are used in large quantities. The increasing introduction and use of more climate-friendly mobility and drive concepts such as methane, hydrogen, e-fuel and hybrid engines is leading to new challenges. Catalysts also play an essential role in the energy transition, in households, restaurants and in the purification of waste- and groundwater. The importance of catalysis in climate and environmental protection is also reflected in the growing awareness of pollutant-free product and process design and is thus directly related to the topics of the energy transition and hydrogen economy (Chapter 1) as well as raw materials, circular economy and CO_2 implementation and use (Chapter 2).

3.1 Emission reduction in mobile and stationary exhaust gas cleaning applications

Vision

» Catalysts are core components in modern exhaust gas purification processes.

» Different and adapted processes and catalysts are available for mobile and stationary applications.

» Drivers of further research and development are the changing raw material base, new sources of emissions and more stringent regulatory frameworks.

In recent decades, many very efficient catalytic methods have been developed for cleaning exhaust gases from internal combustion engines in mobile and stationary applications. As a result, their emissions of carbon monoxide, unburned and partially burned hydrocarbons, nitrogen oxides and particulates have been significantly reduced. The technologies established for this purpose, (diesel) oxidation catalysts, three-way catalysts, NOx storage catalysts and SCR catalysts, are reliably in use. Recently, the challenges of processing the reducing agent ammonia from a urea-water solution for the selective catalytic reduction (SCR) of nitrogen oxides for mobile applications have also been successfully overcome. Today, modern exhaust gas purification systems usually consist of a combination of several of the technologies mentioned. With the expected changes towards more climate-friendly fuels such as methane, methanol, hydrogen and so-called e-fuels, the focus of research will
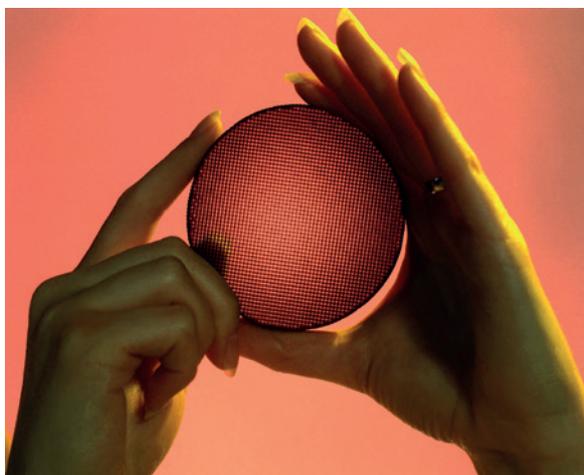

Figure 14: Detail of a catalyst monolith for automotive exhaust gas purification. (© Pixabay / NASA-Imagery)

shift to meet new challenges. These are the reduction of emissions of harmful pollutants such as aldehydes and HCN in very small concentrations and of climate-damaging components in the exhaust gas such as CH_4 and N_2O, for example. New technologies and catalysts are needed to solve this problem. Furthermore, precious metals are used - more than half of the mined precious metals (30% Pt, 70% Pd, 80% Rh), which is critical despite recycling. Since the fuel (H_2, e-fuel) will continue to be burned with atmospheric oxygen in the future, the problem of nitrogen oxide emissions remains.

Gas engines

High engine efficiency, comparatively low pollutant emissions and favorable carbon dioxide emissions make lean-burn natural gas engines an attractive alternative to conventional diesel or gasoline engines. However, incomplete combustion in natural gas engines results in the emission of small amounts of methane. Methane has a strong global warming potential and therefore mandatorily requires an efficient exhaust aftertreatment system. Palladium-based catalysts are considered most effective in low-temperature methane conversion, but suffer from inhibition by the combustion product water and poisoning by sulfur-containing compounds typically present in the gas stream. Rational catalyst design coupled with recent advances in catalyst operation and process control, particularly short rich periods for catalyst regeneration, provide hope that these hurdles can be overcome. The availability of a long-life, high-efficiency exhaust aftertreatment system may encourage the widespread use of lean-burn natural gas engines, which could be an important step toward reducing CO_2 emissions from fossil fuels.

Hydrogen engines

On the road to complete decarbonization of internal combustion engines, a further step is the use of hydrogen as a carbon-free fuel for lean-burn engines, in which NO_x is the main environmental pollutant produced during the combustion process, along with very small amounts of CO, hydrocarbons and ash from the lubricants. In the hydrogen engine, NOx emissions can be significantly reduced by engine control methods; however, an efficient exhaust aftertreatment system is still required to meet the more stringent regulations. Since H_2 is already available from the fuel tank, its use as a reducing agent would be an elegant way to achieve selective catalytic reduction (SCR) of NO_x, especially if the formation of undesirable by-products such as N_2O on the catalyst can be suppressed. Another major challenge in H_2-SCR of NO_x is the required multiple excess of the reducing agent H_2, which is largely oxidized to water under the oxygen-rich

conditions. The search for more selective catalysts is definitely worthwhile in this field.

Hybrid engines

The increasing use of hybrid drive concepts such as the combination of an electric motor with an internal combustion engine is leading to new requirements for exhaust gas purification catalysts, since in hybrid concepts they undergo the cold start phase and transient operating conditions much more frequently, which can accelerate catalyst aging.

Conventional gasoline and diesel engines

The progressive lowering of the legally permissible emission limits, the consideration of further chemical compounds as pollutants to be monitored (e.g. N_2O, CH_4, HCHO), the monitoring requirements and the very low emission limits demanded (e.g. in Euro 7) even under extreme operating conditions require further optimization of existing catalyst systems, particularly with regard to aging, tolerance to poisoning and usable exhaust gas compositions (somewhat with reference to oxygen and water content). In addition, catalysts specifically tailored to further reduction processes are coming into focus, among other things to cover the entire load point range of the engines and/or to use new reducing agents (H2 -assisted NH_3-SCR, NSR-SCR).

Stationary exhaust gas cleaning systems

In addition to engines in mobile applications, exhaust gas purification systems also play an essential role in stationary plants. For chemical plants and production processes, catalytic emission control represents a central task. Waste gases from stationary combustion plants occur in different quantities, concentrations and on a wide range of process dimensions (power plants, small combustion plants, households, etc.). Thus, natural gas continues to be of great importance as a fuel in the sense of a bridging technology for the provision of electrical energy. Legal requirements in households (natural gas heating), restaurants, etc. will lead to further developments of catalytic technologies in the future. For this purpose, catalysts as well as catalytic processes must be developed sustainably and with high demands on long-term stability.

In all areas of emission reduction, the investigation of catalysts under dynamic application conditions (operando spectroscopy) and a theoretical prediction and modeling is becoming more important. In this context, new developments for investigation under challenging exhaust gas cleaning conditions offer the potential of rational catalyst development.

Research needs

» New catalysts need to be developed for the oxidation of methane in water- and oxygen-rich exhaust gases at low temperatures.

» More selective catalysts for hydrogen SCR of nitrogen oxides under hydrogen engine conditions will be developed.

» An improvement in the long-term activity and tolerance of existing catalysts to extremely long startup/shutdown cycles for conventional and hybrid drives is necessary.

» Ccatalysts with long-term stability for the operation of mobile high-load diesel engines and stationary emission sources are to be developed.

» Lower cost catalyst materials are required by reducing the precious metal content.

» Spectroscopic methods for operando investigation of catalysts in exhaust gas purification systems are to be further developed.

» Tracking of the catalytically active sites during the strong and dynamic changes of the reaction conditions should be possible.

3.2 Water and wastewater treatment

Vision

» Trace substances are removed from contaminated water streams by potential-controlled adsorption/desorption on electrically conductive activated carbons and destroyed electrochemically/electro-catalytically.

» Customized zeolites selectively adsorb pollutants from contaminated waters and can be regenerated on site by catalytic oxidation or reduction.

Water is not only the most important foodstuff, but is also a prerequisite for securing our food supply in agriculture. Due to the rising world population, improved living standards and climate change, the demand for clean water will increase in the future and lead to a massive shortage. Therefore, the protection of water resources, in Germany especially groundwater, is of fundamental importance for our quality of life. Already today, numerous surface and ground waters are polluted with a wide range of anthropogenic substances, including nitrates, pesticides and their metabolites, as well as pharmacologically and endocrine active substances. Recently, the substance class of per- and polyfluorinated surfactants has come under increased scrutiny due to their widespread use and extremely high persistence in the environment. Their complete destruction, i.e. their mineralization, requires the use of aggressive reagents and stable catalysts according to the state of the art.

Electrosorption and electrocatalysis

In the development of water treatment processes, a distinction must be made between highly and complexly polluted industrial wastewater with rather punctual occurrence and the diffuse input of large quantities of water via polluted areas, e.g. in agriculture. The former can be treated physico-chemically, the latter practically not. A prerequisite for efficient chemical-catalytic treatment of trace substances in the µg/l range is their prior enrichment. Activated carbons have proven effective for this purpose. Adsorption can remove and concentrate pollutants, but not destroy them. For this purpose, the loaded activated carbons usually have to be thermally regenerated or incinerated off-site. A new approach aims at combining a potential-controlled adsorption of (polar) pollutants on electrically conductive activated carbons with subsequent on-site desorption and electrocatalytic destruction. This combined process is driven by electricity from renewable sources.

Figure 15:Sewage treatment plant for wastewater purification. (© Pixabay / kubinger)

Heterogeneous catalysis in water

One goal of technology development should be to transfer the successes of catalysis in the purification of gases to the purification of water. However, the reaction temperature parameter available in gas phase catalysis is practically unavailable for catalysis in the water phase. All chemical reactions have to proceed sufficiently fast at temperatures around 15°C. In addition, there is the challenge of a so-called water matrix, i.e. reactive water constituents (e.g. chloride or dissolved humic substances) that are present in much higher concentrations than the pollutants to be eliminated. One approach to overcoming these challenges is to use chemically stable, tailor-made adsorbents with a catalytic function. Unlike activated carbons, zeolites can meet both requirements. They often adsorb more selectively and are sufficiently stable even against strong oxidants such as hydrogen peroxide and persulfates. Specific catalytic functions can be implemented by incorporating suitable impurity atoms (e.g., Fe or Cu). The missing degree of freedom *reaction temperature* can be compensated by the parameter *reaction time*: If catalytically active zeolite particles are injected into an aquifer as a form of chemical microreactors, very large 'reactors' and long contact times (reaction times) between contaminant and catalyst are achieved due to aquifer thicknesses and usually low groundwater flow velocities. This in-situ approach to groundwater treatment not only offers cost advantages, it also protects the environment.

Research needs

» New electrode materials for potential-controlled electrosorption of polar pollutants combined with their reductive or oxidative destruction are to be developed. The aim is to develop cost-effective and resource-saving electrocatalytically active materials beyond the benchmark boron-doped diamond coated (BDD) electrodes.

» For the destruction of perfluorinated surfactants, (photo-)chemical and (electro-)catalytic methods and processes have to be developed that require less resources and energy and also function under in-situ conditions and in the presence of real water matrices.

© Pixabay / PhotoMIX-Company
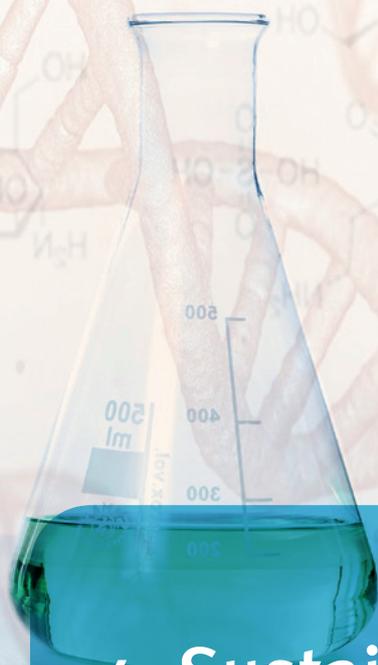
4 Sustainable functional chemicals

Functional chemicals are an important field in the chemical industry and in chemical research. The necessary innovations range from small-scale active ingredients to large-scale polymers. Equally important are innovations in the production of these materials. The range of these highly specialized products with high added value and customer benefits is large, and production volumes vary widely. Applications include specialty polymers in lightweight construction or food and feed products in which vitamins, flavourings, feed supplements or food colorants are used in large quantities. Another important area is crop protection products and pharmaceuticals. The total production of performance chemicals is growing steadily, and the value added is constantly increasing. While mature catalytic systems exist for large-scale basic chemicals, the production volumes of performance chemicals are usually smaller, so that sustainability and efficiency can often be improved. The main reasons for this are short-term market launches, comparatively short product lifetimes and constantly changing markets. For this reason, robust and readily available production methods are preferred, but these do not make ideal use of the raw materials. Catalysis already plays a central role and, with appropriate research, can still significantly improve raw material and energy efficiency in the production of performance chemicals.

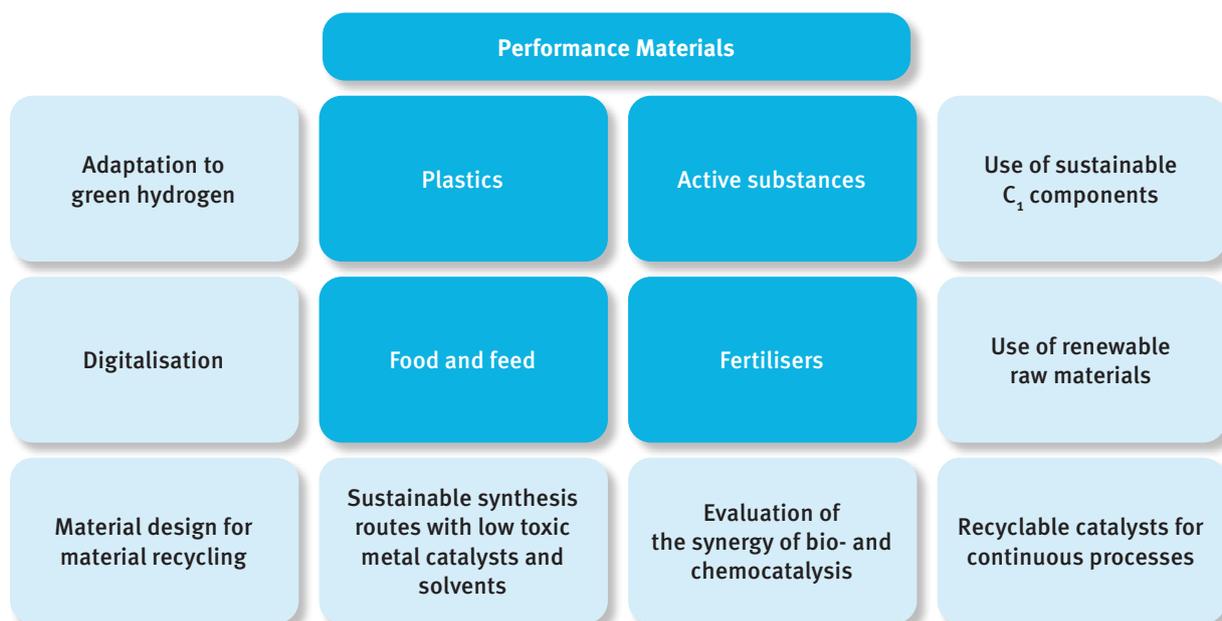| Performance Materials			
Adaptation to green hydrogen	Plastics	Active substances	Use of sustainable C_1 components
Digitalisation	Food and feed	Fertilisers	Use of renewable raw materials
Material design for material recycling	Sustainable synthesis routes with low toxic metal catalysts and solvents	Evaluation of the synergy of bio- and chemocatalysis	Recyclable catalysts for continuous processes

Figure 16: Performance Materials.

Even today, in many performance chemical syntheses, classic organic reactions that have been established for more than 100 years, such as nitrations, Friedel-Crafts reactions and halogenations, are still carried out using stoichiometric amounts of salt waste. Catalysis plays an important role in this process, as it can be used to produce significantly more complex products. Organic fine chemical synthesis sometimes requires cumbersome protecting group techniques (e.g. halogenations, dehalogenations) for the regioselective introduction of a functionality. As a result, established production processes often result in several tons of waste per ton of target product. In the case of active ingredient products, sometimes more than 100 times the amount of waste is generated compared to the active ingredient. An important aspect here is the replacement of solvents of concern, such as halogenated solvents, with harmless solvents.

Catalysis research must develop scalable synthetic implementations in all the areas mentioned to carry sustainable production forms into application. Easy separability and recyclability of the catalysts and reduction of the synthesis steps, even for demanding feedstocks such as renewable raw materials, are crucial. In the performance chemicals environment, biocatalytic and homogeneously catalyzed reactions are used primarily for selective functionalizations. Heterogeneously catalyzed reactions are mainly gas-phase hydrogenations and acid/base catalysis. The flexible combination of these reactions plays a predominant role in linked production processes.

4.1 Plastics

Vision

» The expected billion tons of plastics per year depend less on petro-feedstocks and more on renewable hydrogen, COX-based feedstocks such as methanol, and renewable and waste materials.

» The development and use of biodegradable synthetic materials is becoming increasingly important.

» Catalysis not only opened up the synthesis of new e.g. biodegradable plastics, but also makes it possible to open up new applications for these plastics.

» The circular economy plays a major role in the synthesis of polymers, to this end, the design for recycling and the use of type-pure plastics will be important.

» In the development of new plastics, early feasibility studies with scale-up are important to be able to test large quantities of the new plastics at an early stage.

Polymers are key components in virtually every modern technology. Advanced technologies in communications, mobility, energy storage, drinking water production and food production, as well as the general rise in global living standards, are driving production volumes. Polymer

production is expected to triple to one billion tons in the next 25 years. Unlike other sectors, resource consumption and emissions will increase sharply if development is extrapolated linearly.

The potential contribution of this sector on the way to a society with low resource consumption and low emissions is therefore high and must be taken into account at national, European and global level. Catalysis is a key technology to renew the raw material base, to feed materials to new applications and to reuse plastics.

Regarding the feedstock base, catalytic approaches beyond the established pathways of today's large-scale petrochemical production of monomers are needed. With increasing incorporation of renewable energy, biotechnology and circular economy, the range of base chemicals for polymers will change. Instead of fossil feedstocks, hydrogen from renewable energy electrolysis, small biogenic molecules such as organic acids or amines, CO_2 -based bulk chemicals such as methanol, formaldehyde, formic acid, or direct olefins will play a greater role. This could take the form of new routes to established monomers, for example by electrocatalytic or biotechnological production, but in particular catalysis for the production of new monomers needed for recyclable plastics (e.g. dicarboxylates from renewable raw materials). Efficient catalytic processes to produce such monomers from waste materials - especially from the agricultural sector, and to a lesser extent from fossil feedstocks, are desirable. One established route is the

production of polyethers from CO_2 and alkenyl oxides. Similarly, catalysis can play a key role in the modification of natural polymers such as cellulose, starch, chitin, or lignin to establish new products or more sustainable routes to established products. Catalysts can also be used to explore new applications.

There is a paradigm shift from fossil "cradle-to-grave" approaches of single-use products to reuse, restoration and renewable raw materials, i.e. to a circular economy and a "cradle-to-cradle" approach. Designing plastics for recycling is an open, wide field. Single polymer materials rather than multi-component materials can facilitate recycling. To achieve the desired performance in a single-polymer material, the material properties must be designed, as in the example of "all-polyethylene composites." However, polymer chains that are more amenable to chemical recycling than the inert, pure hydrocarbon chains of traditional polyolefins are particularly desirable. On the one hand, this requires efficient polymerizations to convert the monomers to achieve desirable material properties, but on the other hand, it also requires ways to produce polymers with desirable material properties beyond traditional methods. Examples include the incorporation of carbon dioxide or aldehydes into linear chains.

The handling of plastics after their use will be equally crucial. Instead of landfilling, incineration or conversion to liquid fuels, higher value solutions must be envisaged. Catalytic hydrogenation or oxidation, for example,

Figure 17: Plastic pellets for the production of high-performance components. (© Pixabay / feiern1)

can enable the conversion of secondary groups or inert hydrocarbon chains into valuable low molecular weight chemicals such as (di)carboxylic acids, amines or alcohols. One example of the many challenges in this field is the complete recycling of polyurethanes. Biodegradable polymers with non-critical degradation products could play a key role in this field, as they can not only be degraded in nature, but furthermore, even as a mixture, could be a versatile raw material base for the fermentative production of new starting materials. Sustainability in production and use goes hand in hand with the performance of the materials. Polymerization catalysis that enables new ecologically sound applications is desirable in itself.

These considerable challenges require the full range of transition metal catalysis, acid/base catalysis, oxidation and hydrogenation catalysis, organocatalysis, cooperative effects, biotechnology, electrocatalysis, and other processes still beyond the current state of the art. New and challenging approaches must first be investigated on a laboratory scale and are not suitable for real-world life cycle analysis. However, even in these cases, there should be a realistic perspective for scalability that excludes, for example, high energy consumption, the use of toxic chemicals, multiple reaction steps, non-recyclable stoichiometric reagents, or disproportionately expensive catalysts. In summary, the principles of green chemistry should be followed.

An additional focus is on technical and economic feasibility as well as ecological benefits, all of which must be given. Benchmarking of new materials starts very early. Therefore, to prove marketability, at least technical quantities (a few hundred kg to tons) must be produced with high reliability. Thus, scale-up becomes increasingly important for new polymer materials from the very beginning. All in all, this can be a very long process. It can take years before a new product hits the market.

Research needs

» Efficient catalytic routes to aromatic and aliphatic dicarboxylic acids and diols from plant-based feedstocks are to be developed.

» The catalytic production of (recyclable) polymers and monomers from carbon monoxide and/or carbon dioxide is to be developed.

» The catalytic conversion of polymer waste to valuable products such as (di-) carboxylic acids, (di-) alcohols or (di-)amines is to be developed.

» Tailored polymers are to be developed by using catalysts that can convert new combinations of raw materials into environmentally friendly and cost-efficient streams.

» To reduce by-products and energy consumption towards environmentally friendly technologies, (less dangerous) catalysts must be developed.

» The few catalytic processes that lead to a balanced cost for high-performance polymers need to be expanded.

» Catalytic processes need to be developed for the efficient modification of natural polymers such as cellulose, starch, chitin, or lignin.

4.2 Active ingredients

Vision

» In drug discovery, sophisticated methods for late-stage functionalization are applied.

» In active ingredient production, fewer and more non-toxic catalyst metals are used in non-toxic solvents.

» The catalysts are more selective, tolerant to many functional groups, more stable in use and recyclable.

» Catalysis, in addition to its application in pharmaceutical production, is also used in the field of agrochemicals, as catalyst systems have become cheaper and less toxic.

» Metallo-enzyme systems are used in active ingredient production and are incorporated into cascade reactions.

The development of new active ingredients in the pharmaceutical and agrochemical sectors is essential for health care and nutrition for a growing world population. For example, only new innovative active ingredients can solve the problem of increased resistance to existing antibiotics, but also to crop protection agents caused by new or mutated pathogens.

In the past decades, the search for new active ingredients has predominantly been based on known or existing structures to generate targeted individual (target oriented) or as diverse as possible (diversity oriented) drug candidates. Recently, there has also been an increased trend towards "late-stage functionalization" (LSF) of known active structures. This resource-saving approach has led to a visible shift in research activities at universities. The requirements for catalytic reactions for LSF are fundamentally different from what would be optimal for total syntheses. The ideal reaction for derivatizing a drug activates as many different C-H positions as possible within a highly functionalized molecule and inserts new, biologically relevant functional groups there. A complex mixture of products can even be advantageous if this can be separated chromatographically and then yields several potentially interesting derivatives of the active ingredient at once, e.g., with halogen, fluoroalkyl/alkoxy groups. Chemoselectivity is critical in this type of drug discovery. It is obvious that such methods are mostly unsuitable for industrial synthesis of single active compounds. Once a new active ingredient is identified by LSF, the entire synthesis may need to be redesigned, again requiring catalytic processes that are as selective, sustainable, and waste-minimized as possible. Significant progress has been made in this area: Highly efficient catalysts for activating unreactive leaving groups in cross-coupling reactions are now commercially available, even at industrial scales. However, the efficiency of the expensive noble metal catalysts is at best sufficient to produce expensive pharmaceuticals. For applications, especially in crop protection, the development of non-toxic and cost-effective non-precious metal catalysts based on iron or cobalt, for example, would be an important research goal. In enantioselective synthesis, too, the challenges remain largely unchanged.

Figure 18: Medications in the form of tablets, capsules, and coated tablets. (© Fotolia / nppps48)

The need for future research therefore differs greatly between drug discovery and drug production. For production, aspects of sustainability are increasingly coming into focus, especially reducing the need for high-priced or toxic metals. The price explosion of rhodium in the last years and more recently of iridium due to the decline of deposits, as well as the continuous price increase of palladium, show the low availability of these metals and reinforce the need to deal with them in a sustainable way. Due to the price increase, production processes suddenly become unprofitable. Especially in homogeneous catalysis, a research focus should be to develop new methods and catalysts with higher efficiency (TON>1000) or to replace precious metals by readily available or non-toxic metals as well as to further improve catalyst recycling. In the field of readily available metals, the robustness of the chemistry and a comprehensive understanding of the catalytic mechanisms are important to increase the range of applications of the methods and to avoid problems in the production process. Alternatively, artificial, efficient metallo-enzymes could also be developed to replace noble metal catalysts in processes. Another aspect in catalysis development is the replacement of established but toxic solvents with harmless solvents that are not currently used in production. Furthermore, there is a need for inexpensive and robust methods for enantioselective synthesis, since not only pharmaceuticals but also modern crop protection agents increasingly contain chiral centres, in some cases even multiple chiral centres. To produce plant protection products, more efficient methods for carbonylations and CH activations would also be a valuable asset.

In the field of drug discovery, the focus is not so much on aspects of efficiency as on those of chemical diversity, good predictability of reactions, and availability and user-friendliness of the catalysts. Ideally, catalysts should be stable to air and moisture and tolerate as large a number of functional groups as possible. Examples of desirable selectivity would be the conversion of individual carbonyl groups in the presence of other carbonyl groups, catalytic hydrogenation in the presence of halogens and protecting groups, broader and more predictable applications of CH activation, photochemical and electrochemical catalysis. New methods should be characterized by demonstrating their applicability not only on minimalist model systems, but also on diversely functionalized drug-like molecules. Comprehensive public databases, open-source applications and machine learning could be suitable for improving the predictability of catalytic reactions.

Broadening the spectrum of methods remains important for both drug discovery and production. Innovative concepts such as multinuclear catalysts and coupled cascade reactions of biological and non-biological catalysis could lead to numerous new applications, as could advances in catalytic amide formation and reductive amination with ammonia.

Research needs

» Highly efficient catalysts and robust process steps (TON>1000) need to be developed to minimize precious metal quantities, waste and energy requirements.

» Catalysts and methods for carbonylations, amide couplings, CH activations, enantioselective reactions, among others, need to be further improved.

» Environmentally friendly LSM systems are to be used extensively.

» The influence of solvent systems in catalysis should be better understood.

» Readily available and non-toxic metals for catalysts are to be used in the production of active ingredients.

» The recycling of catalysts must be improved overall.

» Artificial metallo-enzymes are to be developed to extend the applicability of biocatalysis.

4.3 Food and feed

> **Vision**
>
> » Food and feed production is more sustainable with less toxic solvents and fewer process steps.
>
> » Catalysts are based on non-precious metals and are non-toxic.
>
> » The combination of fermentative processes with chemo-catalyzed processes is well advanced.

Food and feed additives are important in combating food shortages. Catalysis makes a decisive contribution to the production of these substances.

The fine chemical industry, which deals with the synthesis of food and feed additives, is in a constant transformation to implement ever more sustainable and efficient processes to meet the pressure for lower production prices and customer demands for more sustainable products. Compounds such as vitamins or colorants are not only used in the food and feed sector but are also used as additives in the pharmaceutical industry or in personal care products. This wide range of applications leads to a product range whose components must be offered in a wide variety of qualities to meet specific customer requirements. Therefore, many compounds are produced via different processes, which in turn start from different starting materials. Examples include chemical synthesis, fermentation, or extraction from a wide variety of raw materials. One important class of substances is amino acids, for which increasing demand is forecast in the pharmaceutical industry and the food

and animal feed sectors. The synthesis of amino acids is mainly carried out using biotechnological methods.

The conflict between the constantly increasing production volume on the one hand and the necessary reduction of the total volume of greenhouse gases - especially CO_2 - can only be resolved if "new" technologies are developed and renewable raw materials are thus made usable efficiently. This will only succeed with a combination of a wide variety of concepts. Catalysis has a central role to play here.

Biotechnology is having an increasing influence. This applies to fully fermentative processes that deliver final products, intermediates of higher complexity that can be converted to the desired product by means of "classical" chemical synthesis, and the production of cheap raw materials. Hybrid processes in particular – the combination of biotechnology and chemical synthesis – hold great potential.

Value creation from waste streams - such as from lignin - will gain in importance. The conversion by catalytic methods towards compounds with higher complexity and purity and enables the replacement of fossil raw materials.

There is a constant need for new or improved metal-catalyzed processes that enable higher selectivity, including enantio- and diastereoselectivity, shorten existing synthetic routes, and/or allow the use of new feedstocks. In addition, catalysts based on commonly occurring elements are increasingly being used to avoid toxic or poorly available metals. More reactive catalysts and/or catalysts with higher recycling rates also enable more efficient production processes that reduce ecological impacts.

The influence of electrochemistry related to sustainable energy and the development of new electrode material are also expected to gain importance.

In addition, there is growing pressure from an environmental perspective to substitute specific reagents and solvents in production processes and to reduce impurities, such as halogenated solvents. This opens applications for new and/or alternative solvents

Figure 19: Feed for livestock. (© Pixabay / guvo59)

such as supercritical fluids. In this context, catalysts are needed that adapt to the changed framework conditions.

Big Data will also expand its influence in the field of catalysis and help to develop more efficient catalysts. Measuring more, more reliable, and more accurate data by means of online monitoring, flow technology and the use of high-throughput screening systems will become increasingly important in this context as new software is developed.

In the future, DFT calculations will allow a deeper understanding of catalysts, encompassing not only fundamental aspects such as the rate-determining step of a reaction, but also complex reaction pathways and mechanisms. Another application will be the modelling of homogeneous, but also heterogeneous catalysts (surfaces). Programs that satisfactorily allow this are still in their infancy but are expected to develop rapidly. Quantum computing and machine learning will play an increasingly important role here.

Research needs

» The trend towards continuous processes will continue. This will require more robust catalysts with a higher degree of recycling.

» More non-toxic catalysts based on common elements need to be developed to further reduce production costs.

» Expanding digitalization to allow more accurate modelling of responses and processes will be important.

4.4 Fertilizers

Vision

» The catalyst systems for ammonia synthesis require less pressure and temperature and thus less energy.

» The catalysts for ammonia have been adapted to renewable hydrogen sources such as electrochemically generated hydrogen.

» New catalyst systems from homogeneous, biological, and electrochemical catalysis have reached a high level of technical maturity.

» The development of a catalyst for the selective decomposition of ammonia was achieved to evaluate the possibilities of energy storage of ammonia.

Ammonia is one of the most important basic inorganic chemicals and the key to industrial nitrogen chemistry. More than 85% of the world's ammonia production is used to make synthetic nitrogen fertilizers. Synthetic fertilizers are responsible for half of the world's food production; without them, it would not be possible to feed today's global population. With a global production of approximately 144 megatons per year (2018), ammonia has the second largest production volume of all basic inorganic chemicals after sulfuric acid. With a growing world population, demand for ammonia is expected to increase by about 12.9% over the next five years (2020-2025).

In addition, ammonia could become even more important in the future as a potential hydrogen carrier for storing hydrogen, but this also requires an efficient way to recover the hydrogen by ammonia decomposition. One goal of current research is therefore to find a suitable catalyst for ammonia decomposition. So far, a catalyst that can be used on an industrial scale is lacking.

Although the process of ammonia synthesis is already highly developed, there is still room for improvement, as even small improvements have a large economic impact due to the very large global production volume. About 1-2% of the world's energy production is used for ammonia production, making it the largest energy consumer worldwide.

Therefore, even a slight reduction in the required process energy as well as process costs would be desirable. This could be achieved by improving existing catalysts

or developing new catalyst systems to improve overall performance and lower the high temperatures and pressures currently required for an efficient process.

At the same time, the environmental impact of ammonia production must be reduced in view of the conversion of our energy system. In particular, the current processes for producing hydrogen emit large amounts of CO_2 and are based almost entirely on fossil fuels. For environmentally friendly ammonia production, hydrogen must be obtained from CO_2-neutral sources, e.g., by splitting water with electricity from renewable sources. However, this change in raw material supply requires an adaptation of conventional catalysts and process concepts.

Alternative routes to ammonia production such as homogeneous catalysis, biological production and electrochemical synthesis are also the subject of current research. These approaches in catalysis need to be developed so that they exhibit high reactivity and selectivity and are suitable for large-scale application.

The main developments of strategic importance for the production and use of ammonia are as follows:

Research needs

›› Optimize the performance of catalysts for ammonia synthesis to reduce the energy demand of the industrial process by lowering the required temperature and pressure.

›› Modelling of the reaction mechanism and prediction of the catalyst composition should be sought based on theoretical calculations with physical and chemical properties for a better understanding of the reaction and possible new catalytic systems.

›› Environmental impacts of ammonia production are to be reduced by using renewable energies for the production process, especially for hydrogen production.

›› Ammonia decomposition catalysts are to be developed for large-scale application to close the loop for the use of ammonia as a hydrogen carrier on an industrial scale.

›› Alternative routes are to be identified for ammonia synthesis (homogeneous catalysis, biological, electrochemical) with new developments/catalysts in an activity range relevant to the application.

›› Catalysts for the production and purification of the ammonia synthesis feed gas are to be optimized. The focus here is on obtaining a stream that is free of pollutants and coproducts in order to optimize the pressure drop in the reactor and to reuse the spent catalyst.

Figure 20: Effective fertilizer production is crucial for food production.
(© Fotolia / doris oberfrank-list)

5 Digitalization in catalysis
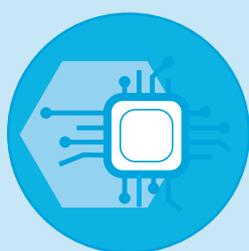
In order to further advance the digital transformation in the technology field of catalysis, a fundamental rethinking is required for the handling of data in catalysis research and development, chemical process engineering and process technology. In order to implement a contemporary and future-oriented approach to digitalization, the various disciplines in catalysis research and technology must be able to cooperate on joint (virtual) working platforms with the support of data scientists and mathematics/computer science and use research data more sustainably and efficiently. The prerequisite for this is the development and application of common data formats and standards. Core elements of these data formats and platforms are, on the one hand, the development of common ontologies and metadata formats accepted within the specialist communities, with which the essential data types can be described sustainably, and, on the other hand, the creation of a common research data infrastructure. It must be attractive for users so that it is actively applied by the research community for research work and development purposes in all aspects. The main goal is to use these tools to redefine the domain-specific technology field of catalysis in the areas of research and development. The paradigm shift to "Digital Catalysis" is to be realized along the data value chain, which is oriented parallel to the real value chain "from molecules to chemical processes".

5.1 The GeCatS initiative NFDI4Cat as a nucleus for "Digital Catalysis"

Vision

» Sustainable research data management is being established in the catalysis community.

» Common data standards and a shared research data infrastructure are used.

» Research data becomes available, analyzable and reusable for the community (FAIR principles)

» Through digitalization, knowledge in catalysis is connected.

» Applied research data management and data science in catalysis are integrated into teaching and education (chemistry, chemical engineering, chemical informatics).

A central role in establishing "Digital Catalysis" is played by the NFDI4Cat consortium initiated by GeCatS in 2019[7]. As a consortium within the German initiative for the establishment of the National Research Data Infrastructure (NFDI), researchers from a wide range of disciplines have been dedicating themselves since 2020 to the implementation of the aforementioned core goals for the research community in the technological field of catalysis. In addition to establishing accepted data standards and setting up a functional data infrastructure, the consortium also aims to establish a "Research Data Management School of Catalysis" and make it available to users. It is intended to convey to the target audience the importance of an integrated and sustainable approach to research data management at the organizational level, but also at the national and international level. The NFDI-4Cat consortium continues to consider aspects such as data confidentiality and intellectual property protection. In this context, it is of enormous importance to differentiate between academic and industrial interests and at the same time to offer universal solutions in order to protect intellectual property and the resulting competitiveness on the one hand, and to motivate the publication and sharing of data on widely accessible platforms on the other. In doing so, NFDI4Cat will help develop reward models to provide incentives for researchers to make data available in digital formats. For example, efforts to make data available could be rewarded quantitatively through the assignment of citable digital object identi-

fier numbers or qualitatively in recruitment processes or in applications for personnel and material funds[8]. Further, NFDI4Cat is discussing the extent to which some buffer time ("retention") between data generation and data sharing may be useful (especially for data generated with public funds) to give data creators control over the intellectual work done with their data. Only in this way can data generators, whether in an academic or industrial setting, derive value from research data and actively participate in the data economy.

Research needs

» Uniform conventions, vocabularies, metadata formats, and ontologies for catalysis research data will be developed.

» A hierarchical repository structure for experimental and theoretical data in the catalysis context shall be provided.

» Tools to support a research data lifecycle (i.e., automated verification of data consistency, accuracy, completeness, and reproducibility) will be provided.

» Advance the development of community-accepted data management plans.

» Reward (reward) models and retention periods to support data sharing and allow the data creator to exploit the data generated in the research process need to be discussed.

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7 Website http://gecats.org/NFDI4Cat-p-20002609.html, access date 2021-02-08

8 C. Wulf, M, Beller, T. Boenisch, O. Deutschmann, S. Hanf, N. Kockmann, R. Kraehnert, M. Oezaslan, S. Palkovits, S. Schimmler, S. A. Schunk, K. Wagemann, D. Linke, A Unified Research Data Infrastructure for Catalysis Research – Challenges and Concepts, ChemCatChem 2021, 13, 1–15.

5.2 Implementation of FAIR principles in the catalysis community

Vision

» Research data are collected and provided in accordance with FAIR principles.

» Legal foundations of intellectual property and aspects of data confidentiality do not conflict with FAIR principles.

» Only prudent implementation of data management plans in line with FAIR principles can lay the foundation for a sustainable digital value chain in the field of „Digital Catalysis".

The NFDI4Cat consortium uses the so-called FAIR principles as a basis for the fundamental developments in the field of "digital catalysis" (Figure 21). These principles are intended to help make the data more usable for the research community.

Figure 21: Illustration of the FAIR principles for handling research data.

The FAIR principles must be met in order to handle research data that can be used sustainably. Of importance here is the findability of the data, to ensure that data and metadata can be found by both humans and machines. This can be achieved, for example, by assigning an identifier such as the Digital Object Identifier (DOI). Furthermore, research data should be archived and made accessible and the protocols used for this should be open, free and universally implementable. In this context, metadata should be made available beyond the lifetime of research data. In addition, FAIR principles are based on data interoperability (interoperable) to ensure that data meet the standards of the catalysis community. Another important point is the reusability of data for further research projects. Here, detailed documentation of the research data must be ensured for universal traceability. The first successful examples of the application of FAIR principles can be seen in the use of digital laboratory journals or electronic laboratory notebooks, online inventory systems and intelligent process control

systems, which are, however, only used to a limited extent by individual research groups or institutions.

Research needs

» The compatibility of FAIR principles in the context of intellectual property and with regard to the data-economic use of data will be examined.

» Appropriate tools to support data sharing according to FAIR principles will be established.

5.3 Use of domain-specific artificial intelligence approaches in catalysis

Vision

» An analysis of research data from all domains of catalysis by algorithms from the field of artificial intelligence is becoming standard.

» Artificial intelligence is used to make predictions about unexplored experimental spaces.

» Domain-specific algorithms for catalyst science based on artificial intelligence that allow analysis of historical datasets (some of which are not available in digital form) -in particular, datasets in text form- have been developed.

In addition to the aforementioned goals and fields of work, one of the important areas of development is the use of artificial intelligence (A.I.) for research and development within the science and technology field of "Digital Catalysis". The main challenge lies in the complex nature of catalysts, catalytic reactions and processes, which often requires an application of artificial intelligence systems adapted to the individual case. Therefore, the development of catalysis-specific A.I. tools based on data provided by the NFDI4Cat consortium is one of the main goals of the digitalization movement in the science and technology field of catalysis. Such tools can be analysis methods and/or simulation techniques that can efficiently analyze data sets and also make predictions about unexplored experimental spaces. In addition to the function of the NFDI4Cat data repository as an expert system, data from other consistent and high-quality data collections are also ideally suited to drive the developments of such A.I. tools in a subject-specific manner. However, not only must sufficiently large data sets be available, but also high-quality data. Data quality can be ensured, for example, by extensive catalyst charac-

terization, a large parameter spectrum and/or reproducibility studies. In this context, high-throughput research also plays a significant role, large data volumes can be generated very reliably and reproducibly.

In addition to its use, for example, for simulation methods in the technology field of catalysis, A.I. can also be used in the conversion of historical, paper-based data sets into accessible, valuable, and usable data formats through natural language machine processing. In the context of language and text processing, A.I. can also help collect information from publications, patents, or internal reports, abstract and process it into a universally usable and accessible data format. In this way, enormous knowledge can be generated for the catalysis community.

Research needs

» Catalyst data will be used to develop and establish catalysis-specific A.I. tools (domain-specific A.I. tools for the catalysis research field).

» The development of appropriate tools to verify data quality in terms of numerical and content data standards is necessary.

» A development and use of domain-specific A.I. tools for speech and text recognition for catalyst science will be undertaken.

5.4 Role of "digital catalysis" in the future: an outlook

Vision

» A holistic digital value chain from molecule to chemical process for processes that include catalysis as an integral component has been implemented.

» Research data are digitally integrated into models for reactor and process engineering for catalytic processes.

» An efficient and community-wide usable data information architecture for catalysis research exists.

» Highly automated and intelligent solutions are available for the laboratory distribution.

» The entire catalysis community in academia and industry is networked.

Digital catalysis" will play a prominent role and lead to enormous advances in the knowledge domain. The core objective here is also to harness advances in microscopic and spectroscopic techniques as well as in theoretical chemistry and in the increasing fundamental understanding of the mechanisms of catalytic reactions throughout the digital value chain. A key challenge is to rapidly

Figure 22:Artificial intelligence tools are used extensively for the catalysis research field. (© Pixabay / geralt)

transfer knowledge gained at the microscopic and laboratory scales to the macroscopic, real-world engineering scale through data-driven work. This is an important concern because in technical reactors the structure of the catalyst may differ significantly from model systems, the state and structure of the catalyst may change under reaction conditions, and catalysts may interact with mass and heat transport processes. One possible method for linking microscopic and macroscopic catalyst systems is to implement molecular models in simulations. However, this approach is currently both technically and computationally challenging. In the near future, digitalization and artificial intelligence methods will open new perspectives for the rapid integration of novel catalysts into technical applications. A first vision is the digital integration of catalyst data into models for reactor and process engineering. Computational platforms need to be established that automatically archive experimental and theoretical information about the catalytic system in the context of the laboratory and the technical reactor and process. In particular, the effects of mass and heat transport and the specific operating conditions must be quickly analyzed and understood. These effects are very specific to the type of reactor, processes, and conditions used. Therefore, computational tools can support rapid analysis and comparison of kinetic data resulting from a variety of experimental studies in different setups and under a wide range of conditions.

Another important aspect in the field of "Digital Catalysis" is the use of digital methods to develop flexible and intelligent laboratory and plant automation technologies. The aim is to run processes and tasks in a highly efficient and highly automated manner.

Several initiatives have already been launched for digitalization in catalysis, and computer tools are currently being developed. Some very valuable stand-alone solutions are myhte – for material, catalyst and process development[9], NOMAD – for building material maps from theory[10], CaRMeN – for archiving, analyzing and deriving reaction kinetics[11,12] and OntoCape - Ontology in Process Engineering[13].

Building an efficient and community-usable information architecture for catalysis research is a daunting task that goes far beyond archiving information in well-defined formats. The ultimate goal of digitalization in catalysis is to enable advanced combination and easy reuse of information and data from many sources, and to ensure rapid but reliable transformation into application tools to provide value to all stakeholders. To date, very valuable functional, purpose-driven, niche digitalization tools have been developed, but typically focused on limited application domains. The scientific community is now beginning to build bridges across scales of length, time, and complexity, with specific research communities gradually overcoming the scattered landscape of existing isolated solutions. Building these bridges, many of which are still in the early stages, is also the focus of the catalysis community, in order to efficiently and beneficially transport data from the molecular level to the reactor and process level and back.

Digitalization within the scientific and technological field of catalysis requires a fundamental change in the handling of data in catalysis research and development, both on a technical and social level. In this context, the NFDI4Cat consortium plays an important role in providing guidelines and solutions for a transition to "digital catalysis". Developments in the field of digitalization in the context of "Digital Catalysis" not only offer the opportunity to generate knowledge from data in a highly efficient way, but also open up a great networking potential in the academic and industrial environment, which can pave the way for a new type and quality of collaboration in a national and global context.

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10 Website https://www.nomad-coe.eu/the-project/centre-of-excellence, access date 2021-02-08
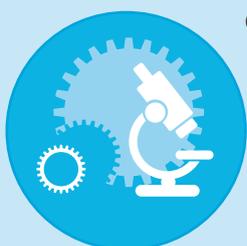
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6 Experimental and theoretical tools for catalysis research

Catalysis has a very strong interdisciplinary orientation in all subfields, both in research and in application. As a cross-sectional discipline, catalysis requires a wide range of methods and tools. Methods and processes from chemistry, materials science and biology are used to develop and produce new and improved catalysts. Artificial intelligence and computer science methods help in the search for new catalysts by developing data-based models relating catalyst structure and reactivity. In order to understand how catalysts work at the atomic level and to develop new catalysts based on knowledge, a variety of physicochemical measurement methods are required, the results of which can be interpreted with the aid of quantum chemical calculations and translated into molecular reaction sequences. For the practical application of catalysis, reactors are needed, i.e. apparatus in which catalytic reactions can be carried out on an industrial scale. Reactor, catalyst and mass and heat transport must be coordinated and form a single unit. Engineering methods are required for this. It is often the case that newly developed or adapted methods or the combination of established but previously independently applied tools open up new research directions and applications in catalysis. Examples are the combination of catalyst synthesis and data-driven modeling or operando spectroscopy directly in catalytic reactors. Some selected tools from this "toolbox" are presented in the following chapter.

6.1 Catalyst synthesis on a laboratory scale and production of industrial catalysts

Vision

» The field of catalyst synthesis in the disciplines of homogeneous, heterogeneous and biocatalysis is benefiting broadly from the trends of digitalization and automation.

» Digital methods occupy a key position as an accelerating engine of progress and are used as a universal tool to tackle problems that were almost impossible to solve in the past.

» Both homogeneous, heterogeneous, and biocatalysis benefit from improved simulation techniques and unified data formats that allow holistic analysis of known and novel synthetic approaches, including activation of catalysts under reaction conditions.

» New analytical methods allow a deeper understanding of the processes taking place during catalyst synthesis.

» Electronic laboratory journals and automated syntheses lead to reproducible and scalable formulations that also use apparatus and procedures on the laboratory scale satisfying a reaction engineering description in the sense of „unit operations".

» The community is actively using means of standardization in combination with digital tools to better manage the complexity in catalyst synthesis and application at all stages.

While the production of molecular catalysts and biocatalytically active enzymes and organisms essentially involves procedural challenges, the synthesis of solid catalysts focuses on the precise synthetic control of "active centers". In all subfields of catalyst synthesis, data-based approaches offer new perspectives.

Molecular catalysts

Catalyst synthesis and the production of molecular catalysts are technologies that have reached a high degree of maturity from the current perspective. Especially in the implementation of theory-based "design concepts" for molecular active components, a high level of development has been reached, allowing to address a variety of complex synthetic-catalytic challenges. Challenges,

which for the field of homogeneous catalysis have still only been partially addressed or remain unsolved, can be summarized as follows:

» **Replacement of expensive and rare metals with cheaper and sustainable alternatives.** Examples can be found here in particular in the field of noble metal-catalyzed reactions. Although the catalyst quantities used are generally comparatively small, their influence on process costs and sustainability aspects cannot be neglected.

» **Replacement of costly synthesis routes to complex ligands by more sustainable and less expensive synthesis methods.** The specific cost of ligand synthesis is usually a relevant factor in molecular catalysts. Alternative lower-cost ligand structures or lower-cost synthesis variants can provide contributions to the cost structure and sustainability.

» **Digital approaches in the synthesis of molecular catalysts.** The use of artificial intelligence methods can open up access to new molecular catalysts with unexpected properties or reveal unconventional reaction pathways and in this way contribute to the replacement of expensive or rare metals with cheaper and sustainable alternatives as well as to the substitution of costly ligands. Data-based innovative development and optimization of the synthesis of molecular catalysts requires the increased introduction of automated synthesis processes, also on a laboratory scale, which have rarely been used for this purpose yet (see chapter 5. Digitalization in catalysis).

» **Use of intelligent robotic systems in automated synthesis.** The introduction of appropriate hardware and software should enable chemical robotics systems (on a small scale) to operate freely in the chemical space and to vary solvents, feedstocks or reaction conditions. Configured synthesis robots are already available. However, for the control of chemical synthesis processes based on "feedback loops" and the use of self-learning algorithms, it is necessary to use or develop a variety of spectroscopic methods and techniques for the acquisition of physical-chemical measured values and to integrate them into the software. This enables analyses of complex reaction mixtures, process control and steering. The results are synthesis concepts being more sustainable, more cost-effective, safer, more reproducible and better scalable to industrial scales with less effort.

» **Development of new process engineering approaches for ligand and catalyst synthesis.** In the synthesis of molecular catalysts, batch synthesis is still the favored route in the laboratory and in technology. New concepts such as flow chemistry have hardly been tested so far despite offering a number of potential advantages and a wide range of applications, especially also for up-scaling issues.

Biocatalysts

Biocatalysts are used as enzymes, whole-cell catalysts or organisms, depending on the field of application. In the development cycle of sufficiently active and stable biocatalysts, two elements usually play an essential role: On the one hand, screening for new enzymes or microorganisms for a specific chemical target reaction or a specific "application target". On the other hand, data-based methods can be used through approaches to structure-activity relationships, which, for example, make use of the contents of sequence databases. For the synthesis and production of biocatalysts, there are a number of challenges that can be formulated as fields of work in perspective:

» **Expansion of the portfolio of enzymes and whole-cell organisms that are being put to industrial use.** Currently, only 100 of about 10,000 natural enzymes are produced and used on an industrial scale. A similar potential exists with microorganisms for whole-cell catalysis - out of 4.5 million species, only about 100,000 are known. This offers broad scope for new developments in biocatalysis in terms of new target reactions and new fields of application.

» **New strategies for the production of tailored enzymes for biocatalysis.** New tailor-made enzymes can be produced, on the one hand, via i) the identification of new wild-type microorganisms, by ii) the transfer of coding DNA fragments into existing production strains, or iii) the targeted modification and optimization of known enzymes. For the targeted modification of known enzymes, the focus remains on two complementary methods: First, rational design approaches that target site-specific mutagenesis, and second, combinatorial approaches based on random mutagenesis.

» **New approaches to process intensification in catalyst production for biocatalysis.** The challenges in particular of the industrial production of enzymatic or cellular catalysts for biocatalysis often lie in small yields and costly product work-up; both factors can limit the space-time yield and have a negative impact on the economy and sustainability aspects of the process.

New approaches in the field of process intensification such as intelligent process control strategies, integrated product reprocessing or the recycling of biocatalysts can open up new fields here.

Solid catalysts

Solid catalysts play a central role in a large number of catalysis disciplines. In addition to classical "thermal" catalysis, examples include electrocatalysis and photocatalysis. Typically, these catalysts are present in the solid state. Research work over the last two decades has shown that the active form of the catalyst is formed under reaction conditions. In addition, the catalyst material undergoes dynamic changes depending on the process parameters. The high reaction temperatures, often applied in classical "thermal" heterogeneous catalysis, are the reason why not only the phase boundary but usually also the volume of the solid is affected by these changes (Figure 23).

The paradigm can thus be understood as the nature of the "active site" at the catalyst surface, which cannot be synthesized directly by methods of preparative inorganic chemistry, but is first formed from a suitable precursor under formation and reaction conditions. Both the atomic structure and the dynamics of the active site are difficult to access analytically under reaction conditions and are therefore poorly known in detail. Moreover, the kinetics of the catalyzed reaction and the kinetics of the catalyst transformation are closely linked via the local chemical potential in the reactor and its temporal variation. Due to the entanglement of the two kinetic processes, structure-function relationships in heterogeneous catalysis are complex and generally cannot be described by purely linear processes. Future synthesis concepts therefore require an integrated approach that includes the selection of optimal reaction conditions and possible reactor technologies from the outset when designing the catalyst material while taking the dynamics into account.

In the synthesis of solid catalysts, the following methodological challenges need to be addressed:

» **New design concepts include the chemical processes involved in converting the product of a material synthesis into the active catalyst.** The thermodynamics and kinetics of the inorganic synthesis of a solid and its transformation into the active catalyst (formation) must be studied as comprehensively as the catalytic reaction itself in the future because of the dynamics of catalysts. Operando methods in microscopy (Figure

23), spectroscopy, and other structural elucidation techniques have shown tremendous potential in elucidating the active state of a catalyst in recent years and must be used extensively. If the knowledge gained in this process is fed back into the development of synthesis toolboxes that incorporate both new and classical preparation techniques, materials can be synthesized in a targeted manner that have the best material chemistry requirements for the formation of a high-performance catalyst.

» **The synthesis of catalysts must be carried out in a scalable manner.** Small batch sizes in academic studies pose difficulties when transferred to larger scales. For example, scientific studies on promising materials or specific nanostructures sometimes render futile because they cannot be considered for catalytic applications under real conditions due to failed scale-up. The synthesis of solid catalysts in the academic laboratory should be carried out at the gram scale with validated and scalable "unit operations" so that all investigations, including functional characterization, can also be performed on one batch. This also increases the validity of characterization data. For successful scaling, the digitalization of the synthesis explained in the following point is of particular importance.

» **The synthesis of catalysts must be carried out in a reproducible manner.** If all possible physical and chemical quantities are measured during individual synthesis steps, such as precipitation or impregnation, they can contribute to the understanding and control of the synthesis. Such an approach will improve the reproducibility of catalyst synthesis and provide new impetus to the advancement of in situ techniques in preparative inorganic chemistry and materials science. The use of sensing and spectroscopy must be accompanied by the development of hardware and software to capture all data and metadata generated during catalyst synthesis in machine-readable standards. This will lead to automated and digital catalyst synthesis (see Chapter 5. Digitalization in Catalysis). A particular challenge in the digitalization of synthesis is posed by those work steps that have so far been carried out mainly manually in academic research, such as filtration, washing, drying or shaping. All work processes as well as all materials and apparatus used must be stringently documented using electronic laboratory notebooks or database systems.

» **Artificial intelligence to master complexity in solid catalyst synthesis.** In addition to improved methods in quantum chemical and multiscale simulation of het-
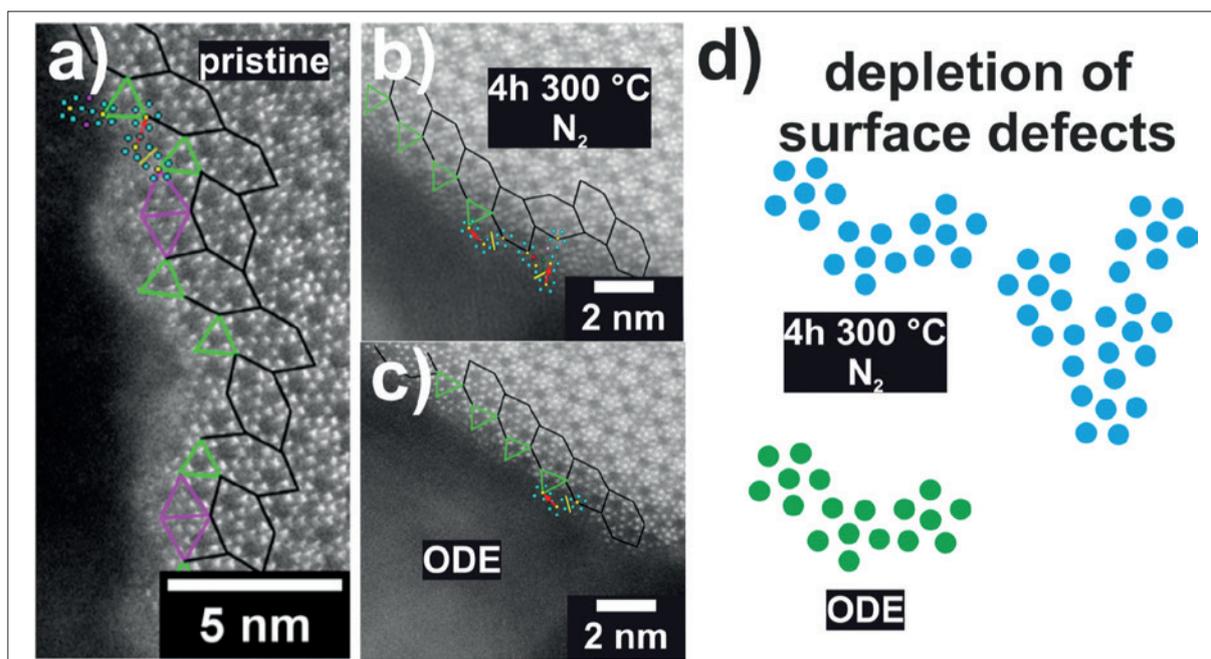

Figure 23: Dynamics of a crystalline defect-rich mixed metal oxide catalyst ((Mo,V)Ox - M1 phase) for the oxidative dehydrogenation of ethane to ethylene, studied by high-resolution quasi-in situ dark-field scanning transmission electron microscopy at identical locations on a) hydrothermally synthesized material, b) after thermal treatment in N_2 atmosphere at 300 ºC for 4 h, and c) after oxidative dehydrogenation of ethane (ODE); The differently colored geometric figures are intended to illustrate the changes in structural motifs of the M1 phase; in d), the transformation of surface defects during the reaction is shown schematically. (© Trunschke/Schunk)

erogeneous solids in catalytic reactions, data-driven approaches based on the analysis of experimental and analytical data become increasingly important. The potentials arising from the combination of both digital approaches lie in particular in unexpected correlations, which are to be found, for example, with the help of algorithms from the field of artificial intelligence (see Chapter 5. Digitalization in Catalysis). The information obtained by means of data analysis provides important target variables for catalyst synthesis (Figure 24). A crucial prerequisite for the application of artificial intelligence in catalyst synthesis is the above-mentioned recording of all process parameters during the synthesis and formation of the catalyst and the archiving of the data in machine-readable form.

In addition to the methodological-conceptual challenges mentioned above, there are a number of sustainability issues in heterogeneous catalysis at the technical level that require solutions:

» **Development and improvement of catalyst production processes in terms of energy and cost efficiency.** The production of solid catalysts goes along with climate-damaging emissions and waste streams. The specific emissions from catalyst production are generally far below the savings in specific emissions that can be achieved by using the catalyst in the process. Nevertheless, in the interests of sustainable production processes and a holistic approach, possible potentials must also be exploited here. Topics that

require new impetus, particularly in the context of industrial catalyst production, are the minimization of specific environmentally harmful emissions and waste streams through:

I)   Efficiency in energy use

II) Avoidance of value losses due to

   a) complex formulations that are difficult to scale (lack of reproducibility on an industrial scale, problems of displayability in industrial assets)

   b) small value-added product yields (due to specific losses in production).

   c) expensive additives and reagents (e.g. template or precipitant)

   d) improved/new analytical capabilities for "in-line" tracking of catalyst synthesis and production

» **Replacement of expensive and rare metals in solid catalysts.** New impetus can come from the development of new concepts for replacing expensive metals with less expensive substitutes. Alternatively, concepts for better utilization of the specific expensive metal content in catalysts should continue to be developed. Keywords such as dispersion enhancement, which offers an opportunity for new manufacturing processes, chemistry or alternative support materials, have their place here, as do approaches for optimizing mass transfer, which can be advanced by developing new forming processes such as 3D printing.
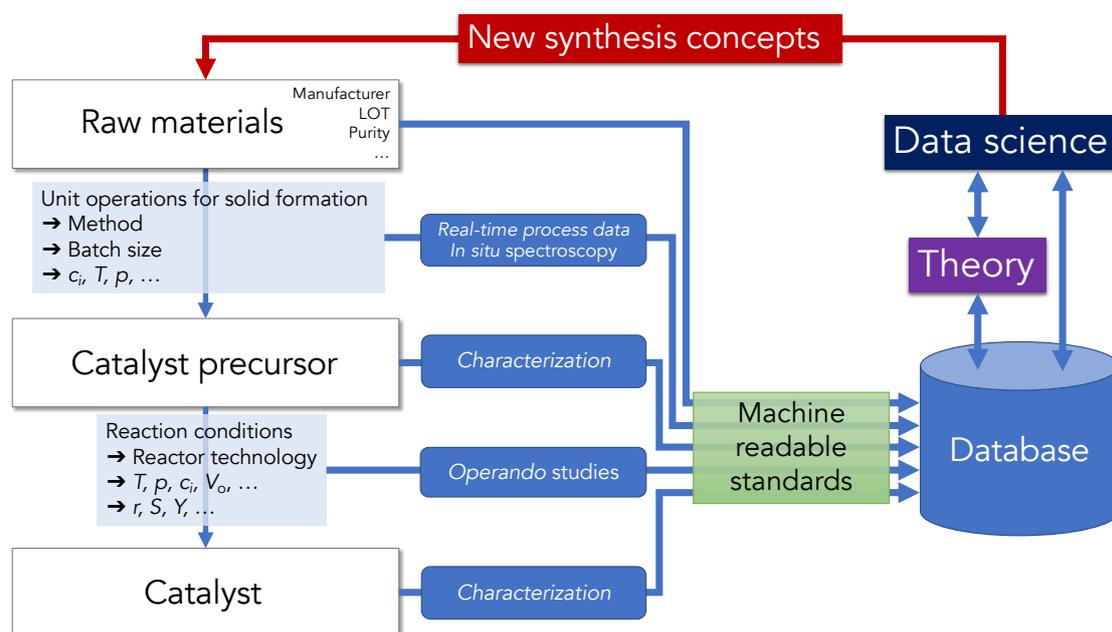

Figure 24: Digital catalyst synthesis. (© Trunschke/Schunk)

A new approach in the context of developing concepts for establishing a "circular economy" (see chapter 2. From fossil raw materials to a cycle of carbon resources) is the conceptual transfer to the field of heterogeneous catalysis. The reprocessing of catalyst waste streams and "spent catalysts" has been practiced for a very long time for the recovery of noble metals, but is new for base metal catalysts. Especially for the metals nickel and cobalt, new integration concepts of "waste streams" from catalysts into emerging value chains around the topics of "urban mining" and battery recycling present themselves. Other alternative approaches are new concepts that anchor the recyclability of the material as a principle in the manufacturing process ("design to recycle"). As an intellectual alternative, concepts of a "second life" for catalyst materials in catalytic and non-catalytic processes with other requirements can be useful. In the sense of a circular economy and the conservation of material resources, such concepts are future-oriented.

Research needs

» **Synthesis of molecular catalysts**
- New digital approaches in homogeneous catalysis need to be developed, based on analytical data and using simulations to identify new lead structures.
- Expensive or rare metals in homogeneous catalysis are to be replaced.
- New and efficient synthesis methods of ligand systems should be made possible.

» **Synthesis of biocatalysts**
- Search for new enzymes and whole-cell organisms for industrial biocatalysis using new experimental and digital methods.
- Digital methods should be used to produce customized enzymes.
- New approaches in biocatalysis on the subject of "process intensification" are to be developed.

» **Synthesis of solid catalysts**
- Deepening an integrated approach to materials synthesis and formation of solid catalysts using modern methods of data analysis and storage in the digitalization of catalyst synthesis.
- Development of new analytical and sensory methods to better capture the synthesis of solid catalysts.
- Development and use of new digital tools that allow stringent documentation of synthesis and analysis data in machine-readable form.
- Development of a consistent interdisciplinary (engineering / inorganic chemistry) approach to standardize and digitally describe „unit operations" in laboratory and technical settings with the goal of improved reproducibility and scalability in solid catalyst production.
- Developing new approaches in the research field of circular economy in catalyst production and recycling.

6.2 Operando investigation of catalysts, X-ray methods and reactor diagnostics

Vision

» Knowledge-based development of new catalytic processes requires an understanding of the structure-activity relationship of catalysts both under idealized laboratory conditions and in engineered reactors with pronounced spatial and temporal gradients.

» Highly sensitive and selective operando methods allow the investigation of active sites in heterogeneously catalyzed gas-phase reactions, but also in liquid phase, e.g. in photocatalytic and electrocatalytic reactors.

» Different operando methods, adapted to each other in terms of spatial and temporal resolution, are combined in one and the same experiment and provide a holistic picture of the course of the catalytic reaction and the function of the catalyst. X-ray methods are particularly well suited for studying catalysts under industrially relevant reaction conditions and allow the investigation of catalysts over all catalyst-relevant length and time scales.

» Imaging techniques of operando X-ray microscopy and operando X-ray tomography provide chemical and structural information of the catalyst in 2D and 3D with high time resolution.

» Laboratory and synchrotron sources are accessible to industrial and academic catalysis research alike, providing infrastructure and personnel for the study of catalytic reactions and the analysis of measured data.

» In the field of reactor diagnostics, suitable operando methods are used to investigate catalysts in reactors from laboratory to production scale. Minimally invasive and non-invasive measurement methods are used to measure concentration and temperature distributions in the reactor and link them to the local, spectroscopically determined catalyst properties.

» Imaging methods such as magnetic resonance imaging are used to measure steady-state and transient concentration, flow and temperature fields in catalytic reactors.

Operando investigation of catalysts

The operando study of catalysts is the analysis of structural and electronic properties of a catalyst with simultaneous measurement of its catalytic reactivity (reaction rate, activation energy, selectivity and product yield). Operando methods are indispensable tools to understand structure-reactivity relationships of catalysts and to develop new catalysts. This knowledge-based catalyst development is becoming increasingly important, replacing conventional methods based on trial and error. Classical operando methods such as FTIR, Raman, UV-vis, magnetic resonance (EPR and NMR), X-ray photoelectron spectroscopy, and transmission electron microscopy have undergone tremendous development in the last two decades. Among other things, a large number of reaction cells have been developed that can be used to study very different classes of reactions.

The increasing importance of catalysis for the energy and raw material transition has led to a shift in the focus of operando methods over time from classical gas phase catalysis to condensed phase reactions, photocatalysis and electrocatalysis. The analysis of surface processes and the detection of single atoms in the presence of polar media and electric fields place new demands on operando method and reaction cells. Since heterogeneous catalysis is mostly a surface phenomenon, operando methods must be sensitive enough to characterize the surface of the catalyst spectroscopically. While FTIR spectroscopy is an established method to study the structure of metal and metal oxide surfaces down to single atoms with CO as the probe molecule, methods such as Surface Enhanced Raman Spectroscopy (SERS) or Infrared Absorption Spectroscopy in Attenuated Total Reflection (SEIRAS-ATR) have been developed to study catalysts in liquid reaction environments (e.g. electrodes). These methods are orders of magnitude more sensitive than conventional spectroscopies and allow selective monitoring of solid-liquid interfaces, electrode surfaces, and surface intermediates. For UHV methods such as XPS and TEM, special sample holders have been developed to study catalysts under near-atmospheric conditions (near ambient pressure NAP). Modern NAP-XP spectrometers have been developed that allow laboratory measurements and are no longer tied to a synchrotron. NAP-HR-TEM instruments are also now available. Sophisticated chip-like Micro-Electro-Mechanical Systems (MEMS) can be inserted into the sample holders of these NAP-HR-TEM and, as catalytic nanoreactors, allow pressures up to atmospheric pressure, temperatures up to 1000°C, or even liquid-phase electrocatalytic reaction conditions. The trend towards miniaturization has also taken hold in magnetic resonance spectroscopy,

leading to the development of EPR and NMR benchtop devices. This evolution continues, e.g. by integrating an EPR resonator on a single mm-sized chip (EPRoC).

To elucidate the complicated interplay between different species and reaction steps in catalytic processes and to compensate for the limitation of single spectroscopic methods, a coupling of different operando methods is required. Ideally, the different operando methods are used simultaneously at the same time on the same experiment to ensure that the different spectra are recorded under exactly identical conditions and exactly identical catalytic reactivity. A variety of method couplings have been implemented in this manner, e.g., XRD/XAS/Raman, Raman/FTIR, NMR/UV-vis, and most recently EPR/UV-vis/ATR-IR/XANES/EXAFS (Figure 25). A common problem with these multi-method experiments is the widely varying time resolutions and sensitivities of the individual methods. To increase time resolution and sensitivity, further work is needed to improve the spectrometers.

In order to be able to transfer results from operando experiments to technical catalysts, it must be ensured that the kinetics and catalytic reactivity of the catalyst under investigation correspond to those in a realistic catalytic reactor. Since the reaction conditions in operando cells often differ significantly from a laboratory plug-flow reactor (sample amount and shape of the catalyst, pressure, temperature, flow, gradients, etc.), not to mention the conditions in a polytropic industrial reactor, research in the field of operando spectroscopy will face a number of challenges in the future.

Research needs

» The gap between industrial reaction conditions and laboratory-scale operando experiments must be closed by ensuring that operando experiments are performed under kinetically relevant conditions without significant influence of mass and heat transport.

» The current time resolution of operando methods, which is in the range of milliseconds to microseconds, needs to be further increased to penetrate the time scale of elementary reaction steps (nanoseconds to picoseconds).

» The local resolution of some operando methods needs to be increased in order to elucidate correlations between local inhomogeneities within individual catalyst particles or along the catalyst bed and catalytic reactivity. While this is already achieved in some operando methods, e.g. in nuclear magnetic resonance or in X-ray and electron beam based methods, other methods, e.g. EPR spectroscopy, still need to be further developed for these applications.

» Software must be developed that combines data acquisition, storage and evaluation with machine learning methods in order to automate experiments and to be able to evaluate the enormous amounts of data resulting from a high spatial and temporal resolution of operando measurements. This data evaluation should be possible on standard PCs (see chapter 5. Digitalization in Catalysis).
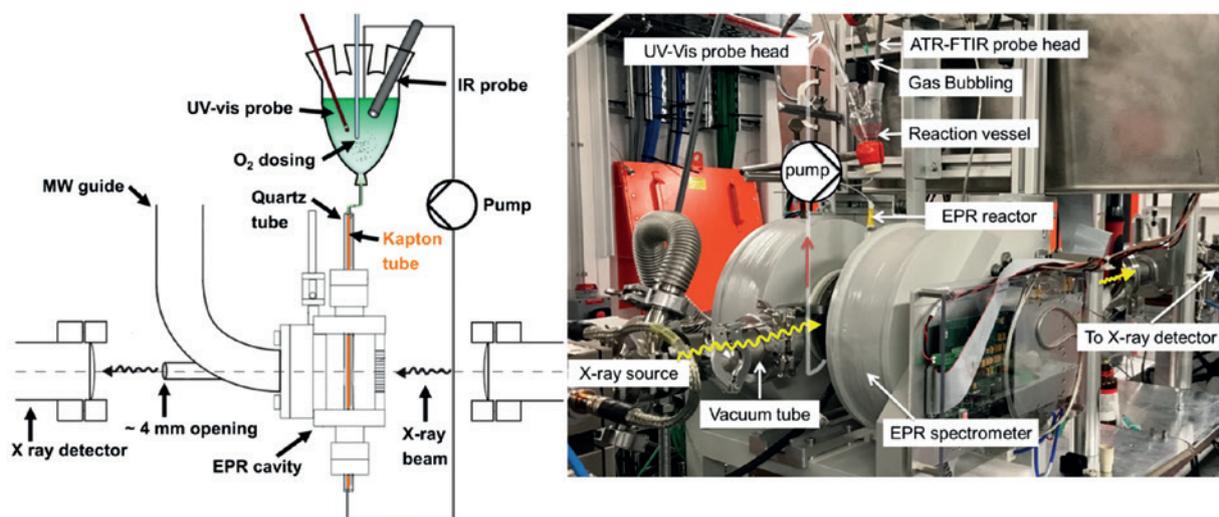

Figure 25: Simultaneous operando EPR/UV-vis/ATR-IR/EXAFS/XANES spectroscopy to study homogeneous selective oxidation of alcohols. (© Brückner[14])

14 J. Rabeah et al. 2020; Chem. Eur. J. 2020, 26, 7395 – 7404. https://doi.org/10.1002/chem.202000436.

X-ray methods

A particularly large and important group of operando methods is based on X-rays, since X-rays penetrate matter comparatively well and one can quasi see inside catalytic reactors. This makes it possible to study the structure and dynamics of catalysts in the reactor. Starting from X-ray absorption spectroscopy (XAS), which is divided into XANES (X-Ray Absorption Near Edge Structure) and EXAFS (Extended X-Ray Absorption Fine Structure), a range of further X-ray spectroscopy methods has been developed and new methods are constantly being added. Photon-in/photon-out methods such as Resonant Inelastic X-Ray Scattering (RIXS), X-Ray Emission Spectroscopy (XES) and X-Ray Raman Spectroscopy have now found a permanent place in the arsenal of operando methods for the characterization of catalysts. XAS is particularly characterized by its broad applicability, providing structural information of both amorphous and crystalline materials as well as liquid phase species. Almost all elements of the periodic table are accessible with XAS. While XAS averages over all atoms in a sample and is therefore considered a bulk method, complementary methods exist with high surface sensitivity. These include XAS, XRD and PDF in grazing-incidence or X-Ray Photoelectron Spectroscopy (XPS). XAS provides critical information about a catalyst under reaction conditions that is needed to understand the activity, selectivity, and stability of the catalyst. This includes the structure and local environment of the active site and its oxidation state, the chemical nature of neighboring atoms and their bond distances and angles, alloy formation, and phase interaction. Other X-ray methods provide in-

formation on particle sizes, particle shapes, nanoscale disorder, alloy formation, metal-support interactions, and adsorbed species. XAS can be combined with other operando methods and the high penetration depth of X-rays allows the study of catalysts in gaseous and liquid reaction environments even at extreme pressures, low or high temperatures, in plasmas or during electrochemical potential cycling. Reaction cells that mimic industrial reactors and operate under near-industrial conditions can be used. The time scale on which X-ray methods can be used ranges from attoseconds (observation of charge transfer processes using free-electron lasers) to weeks and months (observation of catalyst deactivation processes at synchrotron and laboratory sources).

The advancement of X-ray methods for operando investigation of catalysts aims to observe active sites during formation, reaction and deactivation in a spatially resolved manner and with the required time resolution. New and more powerful X-ray sources provide radiation densities that give the above "photon-hungry" methods, the time resolution necessary to observe active sites, and allow surface sensitive methods such as XPS and "bulk" methods such as XAS to be merged. X-ray methods in general, and XAS in particular, have become indispensable tools in catalysis research, and the state of the art can be summarized as follows:

» X-ray spectroscopic techniques allow the investigation of solids, liquids and gases with high sensitivity and on all relevant time scales. They provide information on almost all elements of the periodic table in ac-
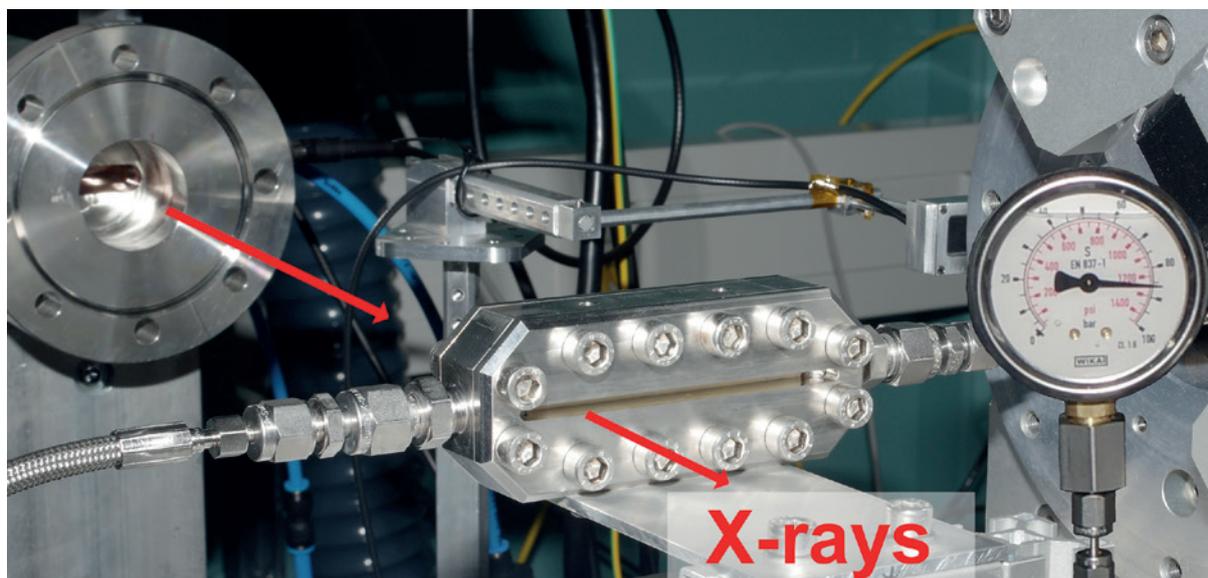

Figure 26: In situ reactor cell for the Operando XAS investigation of the direct synthesis of peroxides at high pressures (setup at the CAT-ACT beamline of the KIT Synchrotron). The manometer on the right side shows the reactor pressure. (© Sheppard/Grunwaldt)

tive centers, catalyst supports, adsorbed species and catalyst poisons.

» X-ray methods provide quantitative information about the concentration, electronic states, local geometry and atomic environment in active sites and ligands.

» In recent years, numerous new X-ray methods have been introduced into catalysis.

» Standard XAS is a bulk method. In order to distinguish active centers from non-involved atoms, the experiment and catalyst must be adapted to this problem. Selective detection of active sites can be achieved e.g. by combining photon-in/photon-out methods, modulation-excitation spectroscopy (MES), diffraction anomalous fine structure (DAFS) and grazing incidence measurement.

» XAS is very flexible and can also be used for industrially relevant temperature, pressure and flow conditions.

Research needs

» Next-generation synchrotron sources must be used to achieve higher time resolutions and enable the application of "photon-hungry" methods (e.g., valence-to-core XES, X-ray Raman spectroscopy, time- and spatially-resolved measurements).

» The sensitivity of methods for detecting species at low concentrations, surface centers, and surface adsorbates needs to be increased.

» New reaction cells need to be developed that allow the study of active site dynamics by operando measurements.

» Spatially and time resolved measurements must be performed on catalytic reactors in operation.

» Catalytic and spectroscopic experiments must be designed that allow the coupling of complementary measurement methods.

» Individual catalyst particles need to be studied with local X-ray spectroscopy and activity measurements.

» Methods such as Modulation-Excitation Spectroscopy (MES), Site-Selective EXAFS, Diffraction Anomalous Fine Structure (DAFS) need to be developed to distinguish different chemical species of the same element (e.g., in the active site and in the uninvolved material).

» X-ray imaging and scattering methods need to be extended with XAS / XES to obtain chemical information, e.g. in X-ray Spectrotomography, Anomalous X-ray Diffraction (AXRD) and anomalous Small Angle X-ray Scattering (ASAXS).

Need for research infrastructure

» Access to synchrotron sources and catalysis experiments needs to be expanded for non-specialists, including the necessary scientific support (e.g., beamlines dedicated to catalysis, beamlines for industry).

» Affordable laboratory spectrometers for X-ray absorption and emission need to be developed.

» Digitalization of data evaluation must occur, through quality-assured data standards, XAS/XES databases, unified evaluation methods on demand by the user, standardization of the sample environment, and development of standardized protocols for measurement procedures, data storage, evaluation, and detection of beam damage.

X-ray microscopy and tomography

Solid catalysts have a very diverse and often hierarchical structure, where structure and chemical function are closely linked. Therefore, it is critical to understand the structure and chemical behavior of a catalyst at all relevant length scales, from the industrial reactor (meter scale) to the active site (sub-nm scale). Ideally, it would be possible to study the active sites of the catalyst across all complexity scales. Characterization methods that provide spatially resolved information, such as microscopic methods, are the approach of choice here. For example, electron microscopy is an established method to study catalysts with extremely high spatial resolution at the nano-scale. Unfortunately, this is only successful for model systems in measurement ranges of a few hundred nanometers, and it is technically enormously difficult to study materials in situ.

X-ray microscopy (XRM) and X-ray tomography are also powerful characterization tools that offer complementary spatial resolution and have recently been increasingly used in catalysis research. Modern synchrotron sources provide X-rays of the highest brilliance and open up entirely new possibilities. For example, X-ray tomography allows non-invasive imaging of the interior of catalyst materials such as pore structure, phases and interfaces. Since X-rays can penetrate matter well, such investigations succeed both in reactors and in individual pellets.

Since X-rays interact with matter in very different ways (e.g. absorption, fluorescence, scattering, diffraction, phase shift), a number of analytical possibilities open up for the characterization of catalysts. X-ray microscopy and tomography combine well-known X-ray analytical techniques such as XAS and XRD, but provide 2D and 3D information, allowing chemical imaging.

With a resolution of 10-20 nm, X-ray microscopy covers the important range between electron microscopy and optical microscopy. Unlike electrons and visible light, however, hard X-rays can penetrate matter very well, so that even larger samples such as technical or industrial catalysts can be examined.

In addition to X-ray microscopy, there are other special X-ray analytical techniques that also have a very high spatial resolution and provide important information for catalysis. These include, for example, scanning coherent diffraction imaging (ptychography) with a routinely achievable spatial resolution <20nm and full-field contrast imaging, which achieves spatial resolutions of up to 50nm on micrometer-scale samples. Both methods are excellent for imaging, for example, the pore structure of catalysts in 3D, which is crucial for mass and heat transport and the accessibility of active sites. Since the pore structure is imaged in 3D, these imaging techniques provide much more information than classical sorption and porosimetry measurements. In addition to the pore network, fine structures, interfaces and heterogeneities become visible in 3D, which is enormously important, for example, when studying electrode materials, mixed metal oxides, supported nanoparticles and solar cells.

A groundbreaking advance for catalysis research is the combination of X-ray microscopy and tomography with operando methods. Here, a variety of structural data of the catalyst can be measured in 3D under realistic reaction conditions, such as gradients in the oxidation state (3D XAS) or the distribution of crystalline phases (3D XRD), and simultaneously the catalytic activity and selectivity of the sample. Such data sets are ideally suited for the derivation of structure-property relationships.

The development of next-generation large-scale research X-ray sources, such as PETRA IV at the national level or ESRF-EBS at the European level, will dramatically improve the experimental capabilities of X-ray imaging in the coming years. It is hoped that it will be
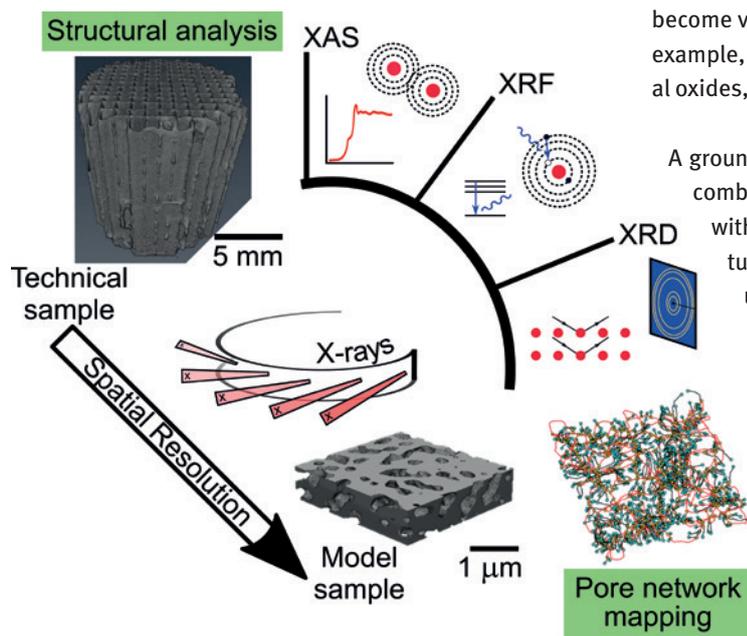

Figure 27: Characterization possibilities by X-ray microscopy and X-ray tomography at a glance. Synchrotron sources allow the study of both model catalysts and technical catalysts using different contrast mechanisms.
(© Sheppard/Grunwaldt)

possible to study catalyst particles or even small reactors with spatial resolutions on the order of 1 nm. Fast imaging methods can resolve dynamic effects on time scales ‹1s, such as gradients in the reactor with periodic modulation of feed composition and temperature. The subject of current research is to develop methods that achieve both high spatial resolution and high time resolution in the largest possible measurement volume. Since the performance limits of X-ray analytical methods can only be exhausted at synchrotron sources, the catalysis community must fight to be strongly represented at the next-generation synchrotron sources and already be intensively involved in the development of these large-scale research facilities.

The state of the art can be summarized as follows:

» Synchrotron-based X-ray microscopy and tomography allow conventional X-ray analytical methods to be used flexibly for chemical imaging.

» XRD tomography allows, for example, structurally complex crystalline materials to be resolved in 3D, and XAS tomography visualizes the distribution of dilute or minority species that are virtually immeasurable with bulk XAS.

» By coupling X-ray microscopy and tomography with modern operando methods, structure-reactivity relationships can be derived in 2D or 3D.

» Unprecedented advances in X-ray microscopy and tomography will be possible with the development of next-generation synchrotron X-ray sources, such as ESRF-EBS and PETRA IV in Hamburg. With these radiation sources it will be possible to measure in larger measurement volumes with higher spatial and temporal resolution than before.

Research needs

» The resolution of X-ray microscopy and X-ray tomography must be increased to the scale of 1 nm.

» Pure imaging must be extended to include „chemical imaging" through contrast mechanisms such as absorption, fluorescence, diffraction, and phase contrast, at all length scales from mm to nm with spatial resolution ‹10 nm.

» The identification and localization of catalyst components must be performed in a single measurement, regardless of whether the materials are amorphous, crystalline or metallic.

» Tomographic spectroscopy and scattering methods, as well as the necessary measurement cells, must be developed for operando conditions in order to investigate structure-property relationships in 2D and 3D.

» A bridge must be built between in situ TEM and operando XRM to allow the study of selected samples at all scales of complexity of catalysis.

» Imaging of the hierarchical structure of engineered catalysts must be performed using multimodal imaging techniques.

» Robust analysis tools need to be developed to extract chemical information from high-throughput and multimodal imaging data.

Experimental reactor diagnostics

Catalytic reactors, in particular fixed-bed reactors in which the catalyst is fixed in space with single-phase or multiphase reaction mixture flowing through or over it, are characterized by pronounced spatial concentration and temperature gradients. If the reactors are operated transiently, these gradients also change as a function of time. Since catalysts dynamically adjust to the local chemical potential in the reactor, strictly speaking, a different catalyst with a different structure and reactivity is present at each point in the reactor. Often, these catalyst dynamics are already manifested by color changes of the catalyst as a function of the local coordinate in the reactor (Figure 28).

The product yield at the outlet of a catalytic reactor is determined by the reactivity of the catalyst at each individual point inside the reactor. The dynamic changes in the reactivity of the catalyst as a function of the local concentration, temperature and flow field result in a feedback
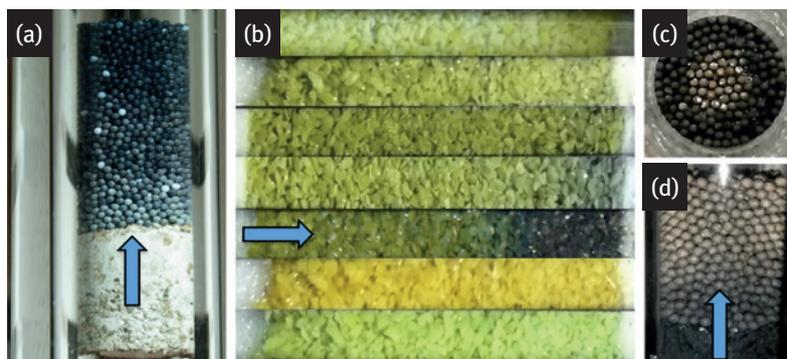
Figure 28: Color gradients of catalysts in laboratory fixed bed reactors as a consequence of the dynamic adaptation of the catalyst to the local chemical potential in the reactor. Oxidative dehydrogenation of ethane to ethylene at (a) MoO /γ-Al$_2$O$_3$ and (b) VO /γ-Al$_2$O$_3$. (c) CO$_2$ reforming methane to Ni/α-Al$_2$O$_3$. (© Horn)

loop that can so far neither be described with sufficient mathematical precision nor measured experimentally by operando methods. This makes the development of catalytic processes very difficult and requires a slow and often years-long groping forward from laboratory experiments to pilot and demonstration plants and finally to production plants.

In order to optimize existing catalytic processes and to establish new catalytic processes more quickly, it is necessary to resolve the temperature, concentration and flow fields in catalytic reactors and to correlate them with the local structure and reactivity of the catalyst. This must be done both by modeling (see Section 6.3. Ab initio and multiscale modeling of catalytic reactions) and by measurement. Classical operando experiments cannot do this, since operando spectroscopy cells are usually built to be optimally adapted to the spectroscopic method (e.g. IR, Raman, UV-Vis, EPR, NMR, XAS, XRD, etc.) and provide gradient-free (low-gradient) kinetic data without the influence of transport processes.

The relatively young research field of experimental reactor diagnostics has therefore set itself the goal of applying spectroscopic and imaging measurement techniques to reactors that are as realistic as possible and measuring the spatial and temporal changes in the catalyst together with the concentration, temperature and flow gradients. This can be done in a minimal invasive way via spatially and temporally resolved sampling in the reactor (Figure 29) or non-invasively via imaging techniques such as Magnetic Resonance Imaging (Figure 30). Minimally invasive methods, for example based on movable sampling capillaries and fiber-optic probes, have the advantage, that they can in principle also be used in technical reactors made of steel and at any temperatures and pressures. The measurement of concentration and spectroscopy profiles in porous single pellets has also been successfully demonstrated. In addition to their wide range of applicability, capillary-based methods of reactor diagnostics are comparatively inexpensive. Disadvantageous is that they somewhat distort the gradients in the reactor due to the influence of the capillary and sampling, provide only one-dimensional information. Also, complete reactor scans take quite a long time, since the reactor must be traversed point by point along the central axis, for example.

Non-invasive and imaging methods such as Magnetic Resonance Imaging provide 2D or 3D information from inside the reactor, in some cases in real time, without disturbing the processes in the reactor by the measurement. Unfortunately, the requirements of imaging measurement techniques on the catalytic reactor to be investigated are very
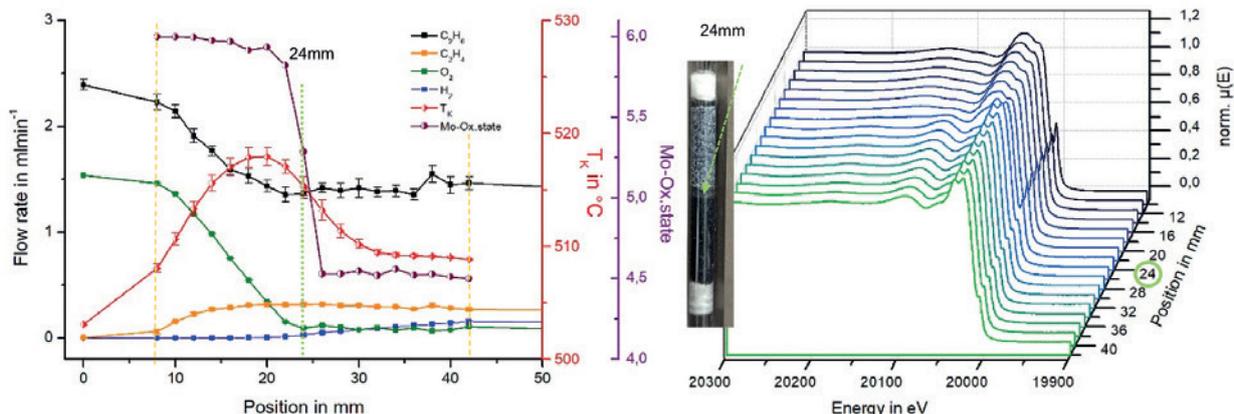

Figure 29: Spatially resolved concentration, temperature, and XANES profiles in a laboratory fixed-bed catalytic reactor during oxidative dehydrogenation of ethane to ethylene on a molybdenum oxide catalyst. (© Horn)

high and require complex design adaptations, e.g. by using non-magnetic construction materials in MRI scanners. Also, there are often tight limits to the reaction conditions that can be investigated, either by the physical mechanism of imaging (e.g. NMR-active nuclei, required spin densities, maximum temperatures) or simply by the design incompatibility of high temperatures and pressures with the sensitive and extremely expensive scanners.

Research needs

» Attempts must be made to adapt further operando methods to realistic catalytic reactors.

» To apply reactor diagnostic methods to industrial reactors, researchers from industry and academia must cooperate closely.

» The application of reactor diagnostic methods needs to be extended to heterogeneously catalyzed liquid-phase and multiphase reactions.

» With the goal of real-time imaging, 2D and 3D measurements must be performed in realistic reactors and single technical pellets with the highest possible time resolution.

» Artificial intelligence and machine learning methods must be applied to spatially and temporally resolved reactor measurements to derive structure-property relationships of catalyst materials.

» Experimentally observed catalyst dynamics must be fed back to rigorous mathematical modeling of catalytic reactors in multiscale simulations.

Real-time magnetic resonance imaging of multiphase and reactive flow systems

The current transition from fossil to renewable feedstocks and the push towards increased resource and energy efficiency requires increasingly detailed process control and thus a deeper understanding of the transport and reaction processes occurring in catalytic systems. Magnetic resonance imaging (MRI) is an imaging technique that provides spatially and temporally resolved measurements of the internal structure and function of three-dimensional samples. MRI is currently used primarily in medical imaging, but is increasingly being used in engineering.

MRI uses strong magnetic fields combined with high frequency fields and magnetic field gradients. Compared to other tomographic techniques, MRI is far more versatile: In addition to the local distribution of phases within the sample (i.e., liquids, solids, and gases), it can quantify a number of sample properties such as flow, temperature, and chemical reactions (see Figure 30).

Until recently, one disadvantage of MRI was the low temporal resolution of several minutes per image. In recent years, the temporal resolution of MRI has been dramatically increased by the introduction of a number of scan acceleration techniques, paving the way for real-time measurements of a variety of process parameters in the field of catalysis research. In the following, these process parameters are briefly discussed.

» **Spatial phase distribution.** The most easily accessible measurand is the spatial distribution of MRI active phases in the sample volume. This type of measurement can be made with high temporal resolution of less than 10 ms per 2D slice through the sample volume. Liquids are the easiest to image, although solids and gases can also be imaged.

» **Flow.** Using appropriate flow coding gradients, MRI can be used to measure the velocity of phases in the reactor. Flow MRI techniques can be used to measure flow fields in multiphase flow systems such as fluidized beds, bubble columns, and trickle bed reactors. Recent advances in scan acceleration have increased the temporal resolution of flow MRI in gas-solid systems by more than four orders of magnitude.

» **Temperature distribution in the reactor.** MRT can be used as a non-invasive thermometer, e.g. to find and measure hot spots or cold spots in reactors. MR thermometry uses the temperature-dependent (NMR) frequency shift of certain MRT-active substances such as water, glycerol or ethylene glycol. A thermal measurement accuracy of ±2 °C and a temperature range of 0 - 160 °C are already possible with a spatial resolution of up to $1 \times 1 \times 1$ mm^3 and a measurement time of a few seconds at a system diameter of up to 100 mm. Further increases in the temperature range and spatio-temporal resolution are feasible and should be further explored.

» **Chemical reactions.** MRI is methodologically closely related to NMR spectroscopy. Combining the imaging gradients of MRI with the spectroscopic approaches of NMR enables the spatial resolution of chemical sample information. This results in a variety of possibilities, such as spatially resolved tracking of chemical transitions. In addition, differences in NMR relaxation parameters (T_1 and T_2) of reactants and products can be used to spatially and temporally resolve reaction

fronts, e.g., in reactions in which the oxidation state changes or in polymerization reactions.

Limitations: In addition to the aforementioned advantages, however, MRI also comes with some limitations. Probably the strongest limitation in the field of catalysis research is the fact that the sample materials must not be ferromagnetic and ideally not electrically conductive. Another disadvantage of the technique is that the cost of MRI experiments is relatively high, and therefore the technique is usually only useful when the desired measurands cannot be measured by other methods. State of the art:

» MRI enables non-invasive measurement of a number of system parameters relevant to catalysis research.

» MRI can spatially and temporally resolve the spatial distribution and flow of phases, temperature distributions, and chemical reactions.

» Recent breakthroughs with scan acceleration techniques have increased the temporal resolution of MRI by several orders of magnitude, evolving the technique from a time-averaged to a real-time paradigm.

Catalysis research is already benefiting from MRI. To further increase its importance for the field, the following aspects need to be further explored:

Research needs

» The temperature range of MR thermometry needs to be extended to study a broader range of catalytic reactions.

» Almost all MR systems are built for medical applications or for chemical structure analysis. To further exploit the potential of MRT in catalysis research, engineering must develop and establish its own MR hardware platforms that are adapted to typical reactor geometries and materials. This includes the construction of high-quality low-field magnetic systems that provide lower-cost platforms and expand access to this key technology.

» Further increases in spatial and temporal resolution are expected from the development of high-performance MR contrast agents and the implementation of scan acceleration techniques such as multiband imaging and image reconstruction based on deep learning approaches.

real-time MRI measures

phase distribution **flow** **temperatur** **chemical reaction**

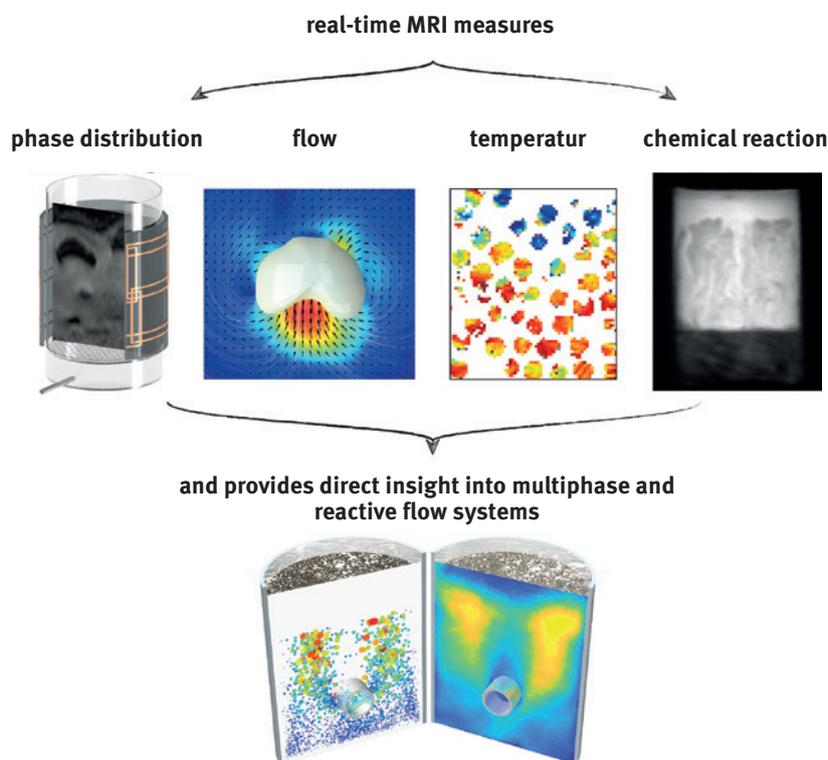**and provides direct insight into multiphase and reactive flow systems**

Figure 30: Overview of some catalysis-relevant parameters of MRI. Solid distribution in a gas-solid fluidized bed (top left). Velocity distribution of the solid phase around a gas bubble (top 2nd from left). Temperature distribution in a solid bed measured with MR thermometry (top 3rd from left). MR detection of an autocatalytic liquid-liquid reaction front (top 4th from left). Gas bubble distribution and particle velocities in a fluidized bed with internals (bottom left). (© Penn)

6.3 Ab initio and multiscale modeling of catalytic reactions.

Vision

» Quantum chemical calculations provide an atomic and molecular picture of catalytic reactions and allow mechanistic interpretation of kinetic and spectroscopic data.

» In a digitized process industry, quantum chemical calculations with predictive potential increasingly enable in silico identification and design of new or improved catalyst materials.

» Breakthroughs also in terms of atomic understanding of catalyst changes under reaction conditions are achieved through close linkage with machine learning techniques.

» New methods and algorithms allow modeling of solvation processes, electric potentials, and non-adiabatic processes as they occur in electro- and photocatalysis.

» More powerful (quantum) computers allow multiscale modeling of even industrial catalytic reactors and allow dynamic feedback of local reaction conditions in the reactor to the atomic level of the catalyst.

Even with very elaborate experimental methods, many details of catalytic reactions cannot be determined, especially not under conditions such as those present in industrial reactors. However, an understanding of catalyst behavior at the atomic and molecular level is essential in order to be able to specifically improve selectivity and yield with respect to a desired product. In heteroge-

neous catalysis, the catalytic centers are usually located on the inner surface of porous solids. Here, phenomena such as multicomponent adsorption and diffusion in the pores must also be described. All of these processes occur in different phases (gas, solid, liquid, and at phase boundaries) and span multiple time and length scales (see Figure 31). The time scales range from femtoseconds for the elemental steps at the active site to catalyst deactivation, which often occurs on the scale of months or years for industrial catalysts. Length scales range from nanometers (active site) to meters (engineered reactors). Appropriate methods must be applied for all time and length scales, which must be seamlessly combined into a multiscale modeling.

On the atomistic scale, quantum chemical calculations are an integral part of catalysis research. With sufficient accuracy for independent predictions, such calculations are traditionally used to establish a mechanistic understanding or to model and interpret spectroscopic data. Over the last decade, this spectrum has expanded greatly towards computer-aided identification of new catalyst materials. The rapid development in this area is due to the ever-increasing functionality, power, and availability of quantum chemical computer programs, explosive developments in machine learning, and the now almost routine linkage to ab-initio thermodynamics concepts and simplified microkinetic modeling. The latter allow a first approximate consideration of reaction conditions, e.g., in stability considerations, or the identification of activity trends within a given class of materials and the associated determination of promising candidates for more detailed investigation.

For heterogeneously catalyzed reactions, density functional theory (DFT) remains the dominant workhorse.
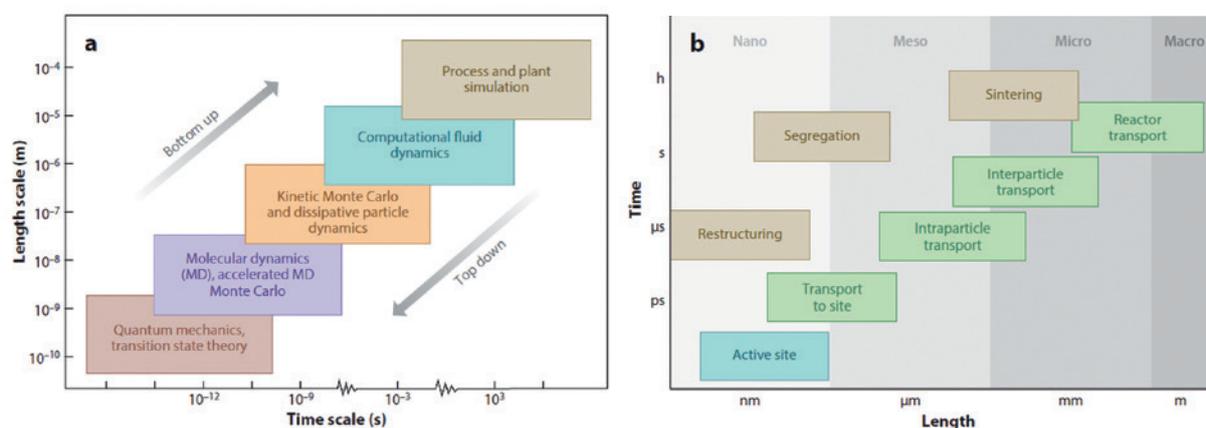

Figure 31: Length and time scales relevant for modeling catalytic reactions. a) Modeling procedures for multiscale modeling of catalytic reactions and reactors. b) Examples of subprocesses to be modeled. (© Keil)

DFT is a quantum mechanical so-called "first-principles method" based on the fact that the total electronic energy of the ground state of a molecule is uniquely determined by the electron density. The method is based on pseudo eigenvalue equations that are solved numerically. For a variety of materials or questions of catalytic interest, DFT simulations with suitable functionals often lead to sufficient accuracy of the quantities to be calculated (e.g., energies). For materials with more localized bonding, hybrid functionals are increasingly established. However, despite continuous performance improvements of software packages and growing power of available computer architectures, the high computational cost remains a critical hurdle for higher-level functionals or for high-precision correlated wavefunction or quantum Monte Carlo methods. Their use is therefore often limited to dedicated validations or to systems where the quantum mechanical description is restricted to a few active centers, as in homogeneous catalysis, or can be limited by using appropriate cluster models or QM/MM embedding methods. Especially for rare earth chemistry, for the calculation of electronically excited states or electronically non-adiabatic processes in photo(electro)catalysis, strong methodological development work is still required.

However, computational time limitations arise even with highly efficient semi-local DFT calculations. Often, this is not because a single calculation is particularly time-consuming, but because a large number of corresponding calculations have to be performed - be it for scanning huge material or configuration spaces or for determining the reaction energetics of large reaction networks with an immense number of possible elementary steps. This is currently fueling broad developments regarding the use of machine learning (ML), especially so-called surrogate models.

Corresponding models provide the same (or well approximated) data-based output as the actual quantum chemical calculations with which they were trained - only many times faster. This output may concern the learning of discrete quantities like adsorption enthalpies or band gaps, or it may concern the learning of total potential energy surfaces as in the case of so-called ML potentials. More comparable in effort to classical force fields, such predictive ML potentials promise significant advances in the treatment of dynamical phenomena and not least in the study of operando changes of active catalysts.

Surrogate models, however, are only one example of a multitude of possible fields of application and connection possibilities of ML and traditional ab-initio-based molecular modeling and simulation. In recent years, a completely new and interdisciplinary community has emerged that is driving corresponding methodological developments and demonstrating the new possibilities in impressive pioneering applications. Central questions also for the next years concern suitable representations, which enable data-efficient learning by encoding physical regularities, as well as the requirements for the simulated data sets (in the future also combined with measurements) used for learning. Here, there is a correspondingly strong overlap or even a pioneering role for the more general efforts in the field of digitalization of catalysis, e.g. within NFDI initiatives such as NFDI4Cat or FAIRmat.

Quantum chemical calculations determine the electronic energy of the molecules at absolute temperature zero. This must still be corrected for the zero-point vibrational energy. For long-range interactions, DFT calculations often introduce a non-classical dispersion energy term based on fluctuations in electron density. With the help of statistical mechanics, the quantum mechanical ener-

ab initio modeling + machine learning in catalysis research

structure

computational spectroscopy

reaction mechanisms

virtual screening

trends und limitations

classification, subgroups, outlier

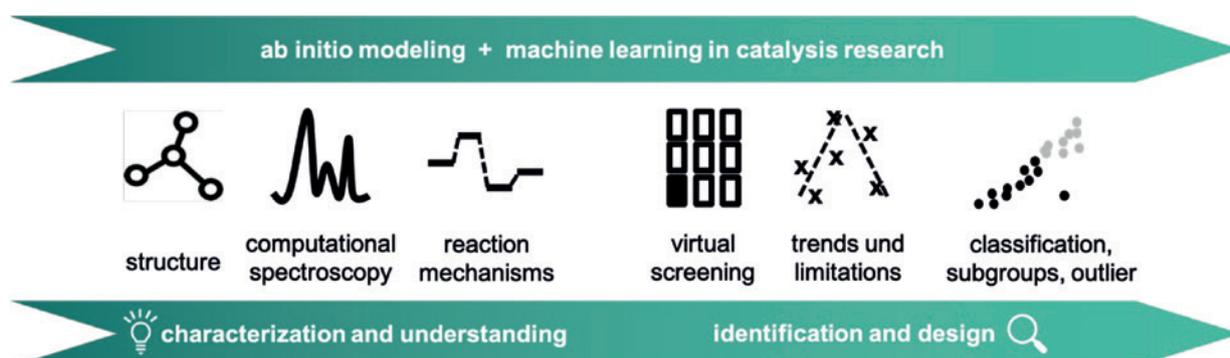characterization and understanding

identification and design

Figure 32: Applications of theoretical modeling methods in catalysis. (© Reuter)

gies can be converted to real conditions in the reactor, in particular its temperature. For this purpose, one determines enthalpies, free energies, force constants, vibrational frequencies and state sums. The search for active sites as a function of reaction conditions (temperature, pressure, reactant composition) as well as phase transitions on the catalysts can become very time-consuming. This is then compounded by electronic interactions between the catalysts and their support materials. Simplifying heuristic assumptions are often made here as well.

When linking with ab-initio thermodynamics and microkinetics as the first stage of multiscale modeling, the main problem is the largely unresolved feedback of the investigated reaction conditions and processes to the underlying quantum chemical calculations. For example, for extended electrocatalysts, solvation effects and the influence of the applied potential on the electron distribution have so far only been taken into account in a highly approximate way, if at all. Likewise, the atomic structure of the active sites in the reactive environment must be assumed or determined indirectly by comparing diverse structural models. The reliability of such a determination depends not only on the structural models considered, but also on the extent to which the real, possibly semi-amorphous structure can be represented within manageable simulation cells. Corresponding feedback limitations are also underlying the use of ab initio-based modeling and simulation approaches for central questions of catalyst aging and regeneration, which has hardly been pursued so far but is urgently needed in the sustainability context.

Since reactions often take place in porous catalyst supports, the multicomponent diffusion and adsorption of the reactants and products must also be calculated using molecular dynamics and Monte Carlo simulation. They determine the actual local composition of the reaction mixture at the active sites, which is crucial for the course of the catalyzed reactions. For reactions in solid-liquid phases, diffusion processes in liquid phase and on the catalyst surface have to be calculated. The different simulations on the various time and length scales are to be linked by connecting theories, with data from the lower level being transferred to the higher level.

Finally, the overall reactor, including the flow conditions occurring within it, must be calculated. For this purpose, molecular simulation programs can be coupled with fluid dynamics programs (CFD) or – in simpler cases – with classical pseudo-homogeneous and heterogeneous reactor models.

Research needs

» Methodological (further) developments are required to calculate more strongly correlated materials as well as electronically excited or electronically non-adiabatic processes in photo(electro) catalysis.

» The dovetailing of ab-initio and ML approaches needs to be further developed, especially for heterogeneous catalysis.

» The reaction conditions must be fed back into the quantum chemical calculations, especially with respect to the electrochemical environment in electrocatalysis or the effects on the structure of the active sites.

» A full temporally and spatially resolved simulation of catalytic processes must be pursued.

» Quantum computing requires the development of new algorithms and computer hardware.

6.4 Catalytic reaction technology

Vision

» The development of new and improved catalytic processes requires the availability and optimal operation of catalytic reactors. For example, the transient operation of catalytic reactors enables the flexible utilization of fluctuating raw material and energy supplies and delivers better product yields than stationary reactors.

» Light and electricity are increasingly used as energy carriers, but also for synthesis. They allow the climate-neutral production of chemical products, e.g. by converting CO_2, H_2O and N_2, and by replacing costly multi-step syntheses with efficient photo- and electrocatalytic processes.

» New photocatalysts and electrocatalysts are based on common and inexpensive elements and are integrated into adapted photocatalytic and electrocatalytic reactors.

» The use of membranes in catalytic reactors leads to higher product yields by shifting the equilibrium position in thermodynamically limited reactions or by increasing selectivity through distributed dosing of reactants in consecutive reactions such as selective oxidations or hydrogenations.

» Removal of inhibiting reaction products from the reaction mixture via membranes increases catalyst life and reduces separation efforts downstream of the reactor, contributing to significant energy savings of catalytic processes.

Periodic operation of catalytic reactors

It has long been known that solid catalysts are not in a steady state during the course of chemical reactions. However, we still have insufficient means to quantitatively describe and predict the dynamically changing catalyst states. Therefore, we cannot sufficiently target dynamic modes of operation to further improve the operation of catalytic reactors.

Continuous flow catalytic reactors are usually designed to maximize desired target variables under steady-state feed conditions. However, due to the deactivation of catalysts and fluctuations of input and operating parameters, transient operation and temporal changes in reactor performance are unavoidable. In order to nevertheless ensure largely constant productivities and product qualities, gradual increases in the reaction temperature as well as specific control engineering interventions are frequently used.

The application of imposed (i.e. forced) dynamic modes of operation by periodic changes of input variables was proposed more than 50 years ago. Although there is now impressive theoretical evidence that substantial improvements over conventional quasi-steady-state operation can be achieved by this means, periodic reactor operation is generally only considered in the chemical industry when steady-state operation is not feasible. Examples include deactivation/regeneration cycles for fast deactivating catalysts, chemical looping processes, and flow reversal reactors (Matros principle). This highly limited application of periodically excited reaction processes is surprising when one considers the numerous cyclic adsorption processes successfully used for the separation of mixtures, such as PSA processes (Pressure Swing Adsorption) or SMB processes (Simulated Moving Bed).

The two main factors delaying further dissemination of periodic modes of operation are generally considered to be the increased process complexity associated with greater equipment expenditure and the insufficient theoretical predictability of process results (e.g. the expected mean values of productivity). However, significant progress has been made in recent years in providing the equipment and automation technology required to implement forced periodic process control strategies, and previous limitations have been reduced.

With respect to the theoretical analysis of forced periodic processes, substantial progress has also been made recently. This is especially true for the NFR (Nonlinear Frequency Response) method, which has become an extremely powerful and readily available tool to efficiently predict time-averaged mass flow rates at the reactor outlet.

Figure 33 illustrates as an attractive example, which can be analyzed with the NFR method, an imposed simultaneous modulation of two reactor input variables, $x(t)$ and $z(t)$. In addition to the appropriate selection of frequencies and amplitudes, phase shifting can be used as another degree of freedom to increase reactor performance. Cyclic operation then leads, after a start-up phase has elapsed, to periodic progressions at the reactor outlet, e.g. with respect to a specifically selectable variable $y_i(t)$. The figure further shows the time average value of the output variable, $y_{i,p,av}$, together with the corresponding value of the steady-state operation, $y_{i,s}$, in which the average values of the two input variables are permanently supplied. An essential finding

of the theoretical work is the fact that, regardless of the kinetics of the reactions taking place, improvements can be obtained for each reaction system by adjusting the phase shift. Provided a valid kinetic model is available, the NFR method allows the best excitation parameters to be identified and the magnitude of the potential for improvement to be estimated.

In summary, the use of forced periodic modes provides a significant and still underutilized potential for heterogeneous catalytic reactions.
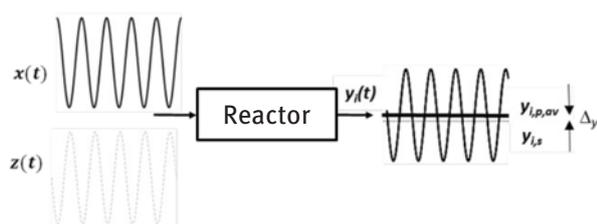

Figure 33: Illustration of forced periodic operation of a reactor for the case when two input variables $x(t)$ and $z(t)$ are periodically modulated using a phase shift. A characteristic output property, y_i (t), then provides a time average value of the periodic operation $y_{i,p,av}$, which can be compared with the value of the corresponding steady-state operation (using the time averages of the two input variables), $y_{i,s}$. Depending on the excitation parameters of the periodic operation, the marked difference to be evaluated, Δy, can be positive or negative. (© Seidel-Morgenstern)

Research needs

» The understanding of the dynamics of heterogeneous catalytic reactions needs to be further improved.

» Reliable kinetic models are required to describe reaction rates and reactor behavior for industrially relevant catalytic processes.

» High-resolution and high-throughput experiments must be performed and exploited for parameterization of dynamic models.

» Machine learning concepts and methods must be used.

» Different modulations of reactor inputs must be evaluated.

» Simplification and further improvement of the availability of NFR analysis is needed (provision of easy-to-use software tools).

» Experimental studies must be conducted to demonstrate the potential of dynamic modes of operation and to validate the theoretical concepts.

Photocatalysis and photocatalytic reactors

Photocatalytic reactions use visible and ultraviolet (UV) light to stimulate chemical reactions. Unlike conventional thermal catalysis, the energy input occurs through the absorption of light of a suitable wavelength by an absorbing material, sometimes in combination with adsorbed reactants. Depending on the actual catalytic system, the absorbing material can transfer the resulting excited electrons and holes to a catalytic material (co-catalyst) or directly catalyze reduction and oxidation reactions on its surface. The reactions can be photon-driven (endergonic reactions, e.g., water splitting) or photoinduced (exergonic, e.g., pollutant degradation). Photosynthesis in green plants is the best-known example of a photon-driven photocatalytic process, in which carbon dioxide and water are converted into carbohydrates and oxygen.

The use of light to drive reactions has several unique features. Light can be viewed as a traceless reactant being consumed during the reaction and disappearing either by absorption or when irradiation ceases. The quantization of the light, as well as the electronic structure of the absorbing materials, results in a very defined activation that often allows for high selectivities. The very high energy content of the photons leads to the formation of electronically excited substances when light is absorbed. They can enter into chemical reactions that are impossible with ground state chemistry and thus with classical catalysis. Light is in principle abundant due to solar radiation, making photocatalytic reactions an important sustainable technology to address the global challenges of climate change and energy transition. Light-driven reactions were studied as the future of the chemical industry as early as the beginning of the 20th century by G. Ciamician. In the past, direct photochemical transformations, especially the excitation and conversion of organic molecules or oxygen/ozone, were the focus of research efforts. More recently, the focus has shifted to photocatalytic processes in which the conversion of reactants involves the transfer of charge carriers to or from the excited photocatalyst. The development and use of both heterogeneous and homogeneous photocatalysts has gained particular attention in the last decade. In this context, photocatalysis opens up new synthetic routes that are very attractive for technical applications and allow long multistep syntheses to be replaced by much shorter photochemical routes. Another important area of research is the photocatalytic conversion of small molecules such as water, carbon dioxide or nitrogen. Regardless of the type of photocatalyst, such reactions open up new chemical pathways that are urgently needed to switch from fossil to biobased feedstocks.

Apart from the use of titanium dioxide for pollutant removal, the commercial use of photocatalysts is rare. Compared to thermal catalysts, photocatalysts must not only have suitable (surface) catalytic properties, but also suitable light absorption properties and suitable positioning of their highest occupied and lowest unoccupied electronic state (valence band maximum and conduction band minimum in semiconductors). In addition, the excited charge carriers must have a long lifetime. The most studied semiconducting oxides TiO_2 or ZnO have the advantage of being inexpensive and comparatively stable. However, they only absorb UV light and have no catalytically active sites for many relevant reactions. This necessitates the use of co-catalysts, which are often based on expensive and rare elements. Alternatives based on widely available elements are currently under development. Molecular photocatalysis usually uses two organometallic complexes in combination, a light absorber and the actual catalyst. The challenge here is to use readily available elements in both.

Despite the high relevance of photochemical reaction engineering for the development of high-performance and efficient photochemical processes, only very few reaction engineering studies have been published. On the one hand, the reaction engineering of photocatalytic reactions is determined by the interaction of light with matter. On the other hand, the same aspects are of importance that are relevant for thermal catalysis, especially heat and mass transfer and thus the synchronization of the time scales of the different processes. This makes the development of high-performance reactors even more complex. Reactors must be designed, on the one hand, to allow light to penetrate and reach the catalyst, and on the other hand, the interaction of the catalyst itself with light must also be taken into account. Therefore, there are different reactor designs, e.g., focused on the use of suspended or immobilized catalysts and light sources. Suspended photocatalysts often exhibit higher activity than immobilized analogs, but require subsequent separation of the catalyst from the liquid phase. This downstream workup can make suspended catalysts unattractive for application.

While harnessing solar radiation is often the ultimate goal, most current studies are conducted with artificial light sources that may or may not be comparable to sunlight. Since the intensity of sunlight, i.e., the con-

Figure 34: Photocatalytic reactor in the laboratory. (© LIKAT/Nordlicht)

centration of photons, is not very high, scaling solar photoreactors is a hurdle. Scaling the receiver area is a very important approach. In addition, photocatalytic reactions are usually carried out under uniform irradiation, which makes the use of artificial light sources very attractive. In terms of reaction technology, artificial light sources such as mercury vapor lamps or LEDs offer the advantages of high and uniform photon fluxes and defined spectral characteristics. Advancements in LED technologies are significantly increasing both the absolute light output and the efficiency of converting electrical energy into photons. The narrow band monochromatic light emission (approx. 20nm spectral width) also enables efficient use of the photons generated. These advantages are increasingly making LEDs the preferred light source.

While several "pure" photochemical processes such as photopolymerizations, photochlorinations or the synthesis of vitamin D have found industrial application, photocatalytic conversions are not yet widely used in industry, with the exception of air and water purification processes. The reason for this is mainly the higher complexity of process development. Due to the lack of experience with the development of industrial photochemical processes combined with the higher technical requirements, photochemical processes are often considered as a riskier alternative to thermal processes. In fact, such an economic assessment is often not supported by hard scientific facts, but is based on an outdated knowledge base in need of improvement.

The Technological Readiness Level (TRL) of photocatalytic processes for most reactions is 3 to 5. However, in some recent work, TRL 8 to 9 and thus industrial implementation could already be achieved for applications with capacities › 1,000 t a^{-1}. Compared to electrocatalysis, the general TRL of light-driven reactions is lower. In view of the great potential, there is a great need for funding to achieve a TRL comparable to electrocatalysis and to maintain and expand Germany's competitiveness in this technology in the future.

In general, light-driven reactions can be considered a viable and highly attractive option to address the challenges of a changing resource base and climate change mitigation, thus enabling the energy transition. To realize the full potential of this technology, the next step must be to translate the fundamental understanding to application. This requires intensive and collaborative research at the interface between materials design, chemistry and reaction engineering. On the way to sustainable photocatalytic processes, the research needs can be summarized as follows:

Research needs

» The scope of photocatalytic reactions and photocatalytically active materials needs to be broadened, both for homogeneously and heterogeneously catalyzed reactions.

» The integration of sophisticated on-line analytics, in situ or even operando, is required for a better understanding of the catalytic process.

» For the technical implementation, scale-up concepts are of great importance and have to be developed.

» The modularization of photochemical reactors needs to be addressed to support the demand for systems with high productivity and scalability.

» Photocatalytic reactions must be adapted to the requirement for flexible and tolerant operation based on a rigorous understanding of the underlying effects.

» All of the above need to be supported by a specific reaction technology that takes advantage of new/additional degrees of freedom provided, for example, by rapid prototyping technologies such as additive manufacturing.

Electrocatalytic reaction engineering

In recent decades, great efforts have been made to meet the increasing demands for clean and emission-free energy conversion and storage technologies. Electrochemical reaction engineering plays a central role in achieving these goals. Electrochemical processes are helping to electrify the chemical industry and are ideally powered by renewably generated electricity. Since the amount of renewably generated electricity in Germany is limited, the processes must be operated more than ever according to the principle of "efficiency first." Another challenge is the necessary flexibilization of the processes, which makes it possible to respond to temporal fluctuations in electricity availability.

The concept of electrocatalysis is concerned with the study of the adsorption properties of the electrode surface in conjunction with the study of the kinetics and mechanism of the elementary processes occurring at the electrode-electrolyte interface. A fundamental understanding of electrocatalytic processes with a focus

on interfacial electrochemistry and material properties aids in the development of novel and improved electrocatalysts. To enable industrial-scale electrochemical engineering reactors and processes, the search for more cost-effective, widely available, highly active, and durable electrode materials will continue to occupy electrocatalysis research in the coming years. In situ and operando spectroscopic and microscopic techniques provide important insights into reaction processes on different time and length scales. For example, changes in the structure and composition of electrocatalyst materials can be studied under quasi-stationary and dynamic conditions to further tailor their material-specific and electrocatalytic properties. The next generation of electrocatalysts will bring improved material, conductivity, catalysis, and mass transport properties.

However, the path to reactors and processes for electrochemical energy conversion and storage also requires development of the interfacial structure of electrode materials to minimize electronic and ionic transport losses. A deeper understanding and optimization of the electrochemical reaction interface will help translate the electrocatalyst materials studied in the laboratory into engineered electrode materials such as gas diffusion electrodes (Figure 35). Hydrogen is an example of how an electrochemical reaction can be very complex. The hydrogen economy (see Chapter 1. Energy transition and hydrogen economy) is inevitably governed by two reactions: the hydrogen evolution reaction (HER) and its reverse reaction, the hydrogen oxidation reaction (HOR) in an aqueous system. HER plays a key role in numerous technologically important areas such as water and chlor-alkali electrolysis, metal deposition, corrosion and fuel production e.g. CO_2-electroreduction. For more than 70 years, HER has been used as a fundamental model reaction system to study the catalytic properties of electrode materials with kinetic rates for the formation

and oxidation of molecular hydrogen under acidic and alkaline reaction conditions. The tremendous loss of electrocatalytic activity of the platinum group metals for HER/HOR from acidic to alkaline environments is poorly understood to date. Other examples of electrochemical reactions where electrocatalysis can provide promising alternative and more efficient pathways include: electrochemical CO_2 conversion to valuable products such as syngas, hydrocarbons, alcohols, etc., electrochemical N_2 reduction to ammonia, electroorganic synthesis, and more.

In addition, mass transport in the cell, the resistances of the cell components and the scalability of the processes must also be examined in more detail in order to arrive at a viable concept. The development of the oxygen depolarized cathode for chlor-alkali electrolysis by Covestro represents a milestone in the development of gas diffusion electrodes for industrial applications. The innovative falling film concept found a way to enable stable operation of the reactor without flooding the gas diffusion electrode. Similar challenges will be faced for scaling up CO_2 reduction or even electrochemical ammonia synthesis. In addition to the gas diffusion electrode, the ion exchange membrane is a key component of an electrochemical reactor. For CO_2 reduction, for example, the use of an anion exchange membrane is particularly desirable because it allows a cell design without electrolyte channels and thus positively influences energy efficiency. However, the insufficient selectivity of the membrane limits the breakthrough of the technology. The anion exchange membrane can also revolutionize water electrolysis, as the development of a stable, high-performance membrane could replace iridium as an anode catalyst with more readily available metals such as nickel. Further research is also needed in the field of cation exchange and bipolar membranes to optimize selectivity, stability and conductivity.
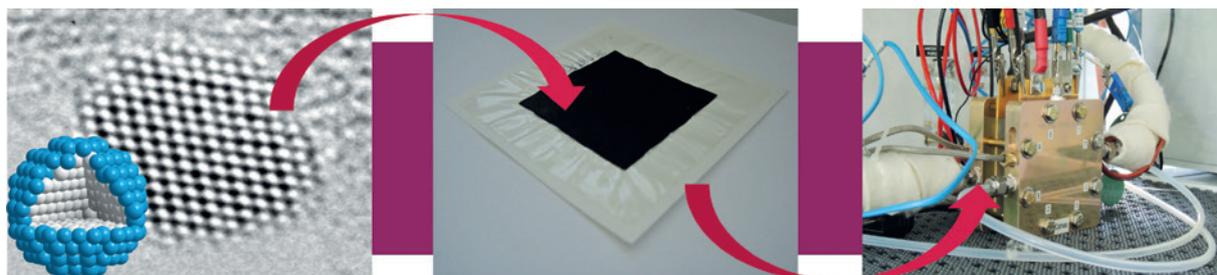

Figure 35: Consideration of materials and engineering aspects for electrochemical reactions from the nanoscale to the cell scale. Left: High-resolution transmission electron microscopy image of a catalyst particle with a core-shell structure; Center: catalyst-coated membrane; Right: electrochemical test cell.
(© TU Braunschweig, Institut für Technische Chemie - Technische Elektrokatalyse)

Biorefineries can contribute to replacing fossil raw materials with renewable ones. The coupling of electrochemistry and biorefinery can combine the advantages of both technologies. For example, products from a fermentation process can be directly processed into valuable materials in an electrochemical process. For this purpose, mass transport at the electrolyte-electrode interface in particular is a key challenge: the product concentration in fermentation broths is often relatively low. In order to nevertheless obtain a high current density in a downstream process, mass transport can be positively influenced by structured 3D electrodes. In this context, additive manufacturing enables new approaches to electrode and reactor design as shown in Figure 36. Processes such as selective laser sintering (SLS) can open up unimagined possibilities in terms of electrode geometry, so that mass transfer at the electrolyte/electrode interface can be multiplied. With new processes in additive manufacturing, the porosity of the electrodes can additionally be controlled in a targeted manner, thereby achieving larger active surfaces. Subsequent functionalization of the surface is accessible, for example, by coating. Furthermore, additive manufacturing methods make it possible to develop completely new reactor concepts that no longer depend on planar or tubular electrodes and membranes.
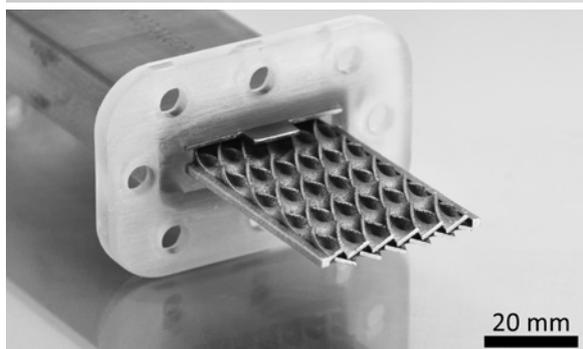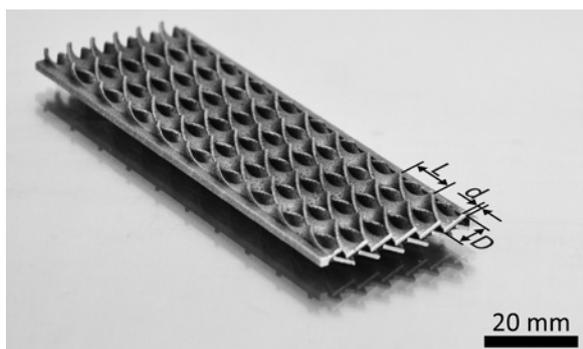
Summary state of the art:

» Electrocatalysis and electrochemical reactions are the main drivers for both electrochemical energy systems and electrochemical chemical manufacturing.

» The combination of material properties and reactor or process characteristics is the key to an optimized reactor design on a technical scale.

Research needs

» The optimization of the electrochemical reactor must be holistic, i.e. taking into account the electrodes, membranes and process parameters (e.g. p, T).

» Scalability of gas diffusion electrodes and reactors must be pursued.

» The stability, conductivity and selectivity of ion exchange membranes must be improved.

» Electrochemical processes need to be integrated into biorefineries and linked to local sources of CO_2 and N_2.

» Mass transfer in an electrochemical reactor and within the gas diffusion electrode must be understood.

Figure 36: Electrode designed as a static mixer produced by 3D printing. (© Richter)

Membrane reactors in catalysis

In today's processes, the separation of reaction products after catalytic synthesis processes is downstream of the synthesis and in many cases requires more time and energy than the catalytic reaction itself. Membrane separation processes consume significantly less energy than thermal separation processes and are therefore more cost-effective. If process conditions and membrane materials permit, it may be possible to integrate membrane separation directly into the reactor, thus coupling the catalytic reaction with mass separation. Such "membrane reactors" allow the chemical equilibrium of the reaction to be shifted, resulting in higher conversions, selectivities, and yields. Strategies for this include selective separation of a reaction product in the reactor or locally distributed addition of a reactant across the membrane.

Although these principles are well known, membrane reactors have hardly been used in industry to date. However, possible applications would be especially for catalytic reactions that take place under harsh conditions and for which inorganic membranes would be used. Promising reactions that can be carried out in membrane reactors include the synthesis of energy carriers such as methane or methanol from renewable hydrogen and carbon dioxide as part of PtG/PtL/PtX/PtCh processes. In these reactions, water is formed as an undesired by-product, which can be removed from the reaction mixture directly after formation via a water-selective membrane. This both shifts the equilibrium to the side of the desired reaction product and minimizes the deactivation of catalysts, e.g. Cu/ZnO for methanol synthesis, which are attacked by water. Modeling work has already demonstrated the advantages of membrane reactors for methanol synthesis. Another example of a promising application of membrane reactors is the steam reforming of methanol with removal of hydrogen through the membrane. Both processes are shown schematically in Figure 37.

One challenge for the use of membranes in catalytic reactors is to harmonize the catalyst performance and the separation performance of the membrane. This requires, above all, close contact between the catalyst and the membrane. As a first step in a reactor development, the catalyst can be positioned inside the membrane in the form of a fixed bed. In a second step, the catalyst can be applied to the membrane as a thin layer. The best contact between catalyst and membrane occurs when the catalyst is placed directly into the membrane, i.e. when working with a catalytically active membrane. All three process variants are currently being investigated in ongoing research projects.

While the catalysts for many processes have already been developed, the available membrane materials do not yet meet all requirements, such as high selectivity for product separation or reactant feed or sufficient stability to process temperatures, pressures and media. In the field of porous membranes, inorganic molecular sieves on porous ceramic support materials are already showing promising results. Another alternative are "dense" membranes, in which mass transport is based, for example, on the conductivity of oxygen ions or protons. An industrially relevant example is the controlled and uniform supply of oxygen from air via a membrane in a reactor for the catalytic partial oxidation of hydrocarbons, e.g. methane, to synthesis gas. The production of synthesis gas by catalytic partial oxidation of methane is an important process step in the industrial production of artificial fuels and chemicals.

Summary state of the art:

» Coupling catalytic reactions with membrane-based separation processes, such as selective separation of a reaction product or selective feeding of a reactant, can increase the efficiency of catalytic processes.
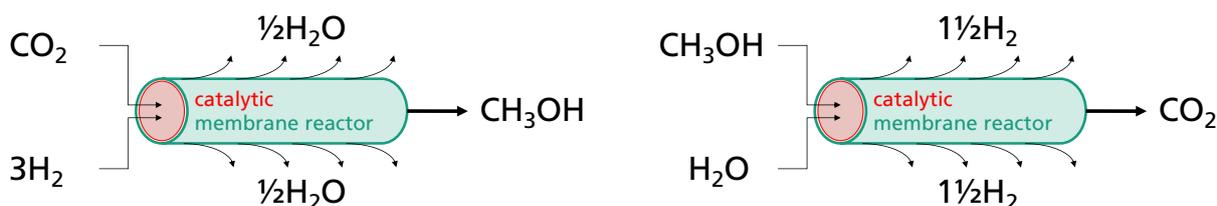

Figure 37: Application of membrane reactors for methanol synthesis (left) and steam reforming of methanol (right). (© Fraunhofer IKTS / J. Richter)

» The principle of catalytic membrane reactors has been known for a long time, but has hardly been used industrially so far because the increased production efficiency does not yet outweigh the additional costs for the development and use of membranes.

» Promising and stable membrane materials have been developed that can be adapted to the respective catalytic processes.

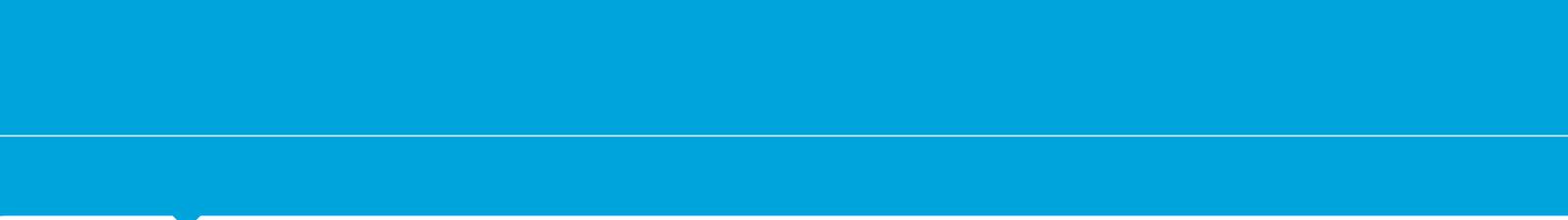» By using membranes, new highly integrated reactors and plants can be developed.

Research needs

» Ways must be found to optimally link the catalytic processes and the mass transfer processes across the membrane.

» Catalyst formulations must be developed with which membranes can be easily coated.

» The selectivity of the membrane must be adaptable to the particular catalytic process.

» The range of applications of catalytic membrane reactors needs to be extended, e.g. to synthesis processes in fine and specialty chemicals.

» The range of available membrane geometries must be extended and must range from monoliths to capillaries

» The scalability of membranes and catalytic membrane reactors must be improved, especially in the direction of scaling up at economically justifiable costs

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