

ROADMAP FOR CATALYSIS RESEARCH IN GERMANY

# CATALYSIS

A key technology  
for sustainable economic growth

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## Preface

Catalysis is the single most important interdisciplinary technology in the chemical industry. More than 85 % of all today's chemical products are produced using catalytic processes. However, the importance of catalytic processes is not limited to the chemical industry. They also play a central role during the processing of raw materials in refineries, during the production of energy e.g. in fuel cells and batteries, as well as in terms of climate and environmental protection.

Catalysis research is a highly interdisciplinary field, and it is characterized by the fact that major economic potential is always attached to the results of the research. One example worth mentioning here is the Haber-Bosch ammonia process with a catalyst which was developed by Alwin Mittasch at the start of the last century. Today, it would not be possible to feed the world's population without this process.

Germany has played the leading role in the field of catalysis research for over 100 years – a position which has to be secured and strengthened. This will require not only highly qualified and motivated catalysis research scientists, but also the availability of appropriate research funding.

The Roadmap for Catalysis Research in Germany provides an outline for future priority areas of research and for research funding and promotion in the field of catalysis in Germany. This 3rd edition of the roadmap has been revised on behalf of the German Catalysis Society (GeCatS) and is an update of the Roadmap for Catalysis Research in Germany which was published by the Competence Network Catalysis (ConNeCat). The document has been revised by select experts in the relevant fields and updated in order to take recent developments into account. We make no claim that this document is complete, but hope that it will be used as a basis for discussions about applications in catalysis research which have a particularly high innovation potential.

This roadmap can be downloaded from the website of the German Catalysis Society at [www.gecats.de](http://www.gecats.de).

## 1. Securing supplies of raw materials



Today, the issue of securing supplies of raw materials to the chemical industry cannot be isolated from the context of the energy industry.<sup>1)</sup> All of the raw materials discussed below are also energy carriers, and only a small proportion in each case is used for the production of materials. Consequently, higher-level strategies should focus on reserving reactive raw materials for material production cycles and using those which are less easy to activate for energy production. Finally, any evaluation of alternatives to raw materials must take into account what the hydrogen content of these materials is in comparison to the products manufactured from them. The use of low-hydrogen raw materials requires access to hydrogen which is independent of fossil sources.

### 1.1. Crude Oil

For more than 50 years, crude oil has been one of the central primary energy carriers – and this is set to remain unchanged in the medium term future. However, limited availability and deteriorating quality will ultimately reduce its contribution to the overall energy supply mix. The major challenges faced by chemical processes to utilize the oil which is produced relate in particular to a shift in quality towards oil types which have a lower hydrogen content and which are less pure. Given the ever

more stringent environmental legislation which has to be satisfied, this change cannot be managed with the aid of conventional technology. New catalytic techniques in conjunction with innovative reaction engineering will form the necessary basis on which these new raw materials can be integrated in existing refineries. The key to success will be the redistribution of hydrogen between molecules, selective hydrogenation and the purging of heteroatoms and metals.

In an ideal scenario, crude oil should predominantly contain molecules with a mean hydrogen to carbon ratio of just below a value of two. However, the ratio of hydrogen to carbon in molecules in real crude oil is often noticeably lower than this, and the molecules also contain significant quantities of oxygen, nitrogen, sulfur and phosphorus, as well as small quantities of metals like nickel, vanadium, arsenic or mercury. If ways are not found to improve the exploitation of existing sources then the quality will shift towards heavier oils with a lower H/C ratio and large quantities of impurities.

In 2007, confirmed global reserves were estimated at approximately 1240 billion barrels<sup>2)</sup>, of which around 61 % is in the Middle East. Based on a worldwide average daily consumption of 85 million barrels, the ratio of reserve to production is slightly more than 40 years; the available refinery capacity is increasing slightly and is now around 88 million barrels per day.

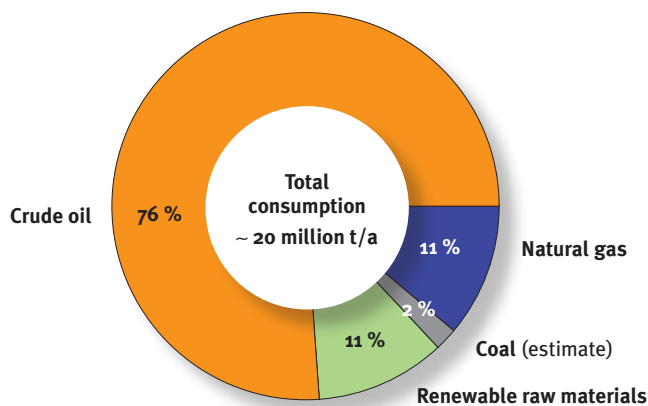


Figure 1: Use of raw materials in the chemical industry (Source: VCI)

<sup>1)</sup> Policy document „Rohstoffbasis im Wandel“ (The changing nature of the raw material base), DECHEMA, DGMK, GDCh, VCI, January 2010

<sup>2)</sup> BP Statistical Review 2008

Looking back, a thousand billion barrels of crude oil have been produced over the last 150 years ( $1 \times 10^{12}$  barrels). It should be noted that, as a general rule, only slightly more than 35 % of the capacity of any given deposit is actually recovered. There are several strategic approaches for the time after this:

### Crude oil recovery

#### a. Enhanced oil recovery from existing oil fields

The current state of the art is to use physical methods to reduce the viscosity of the crude oil and to increase the pressure in a deposit. This allows the potential yield to be increased to 60 %. The yield could be significantly increased if it attempts to use catalytic methods like hydrogenation, hydrocracking and hydrogen transfer to crack high-molecular hydrocarbons under the prevailing conditions of a deposit or to change the H/C ratio of the hydrocarbons in the molecules were to succeed.

#### b. Diversification into alternative crude oils

Oil shale and oil sand are the most important alternatives to conventional crude oil deposits. Whilst oil shale is a „young oil“, oil sands are bacterially infected deposits with a low H/C ratio which are near to the surface. At present, oil shale is thermally matured for years through a process of hydrogen redistribution. Catalysts which accelerate this process could make the processes commercially viable.

### Exploitation of crude oil

Crude oil is distilled under normal and reduced pressure into different fractions, which are then processed into useful products in the refinery. With a given refinery configuration, the quality of the crude oil determines the production quantities of the various products. As the specifications of the products (energy carriers for mobile and stationary applications, lubricants and chemicals) and the demand are given, the quality of the crude oil determines the outlay and work involved in production. Consequently, any change in the quality of the crude oil results in a major shift in the scope and nature of individual processes in the refinery, and this represents a huge challenge for the catalytic process.

- The reduction in the H/C ratio of the crude oil demands preferably comprehensive hydrogenation at an early stage of the chemical process. The additionally required hydrogen must be produced from fossil or regenerative sources.

- Larger quantities of the (heavier) hydrocarbons need to be cracked (resin cracking, fluid catalytic cracking, hydrocracking). Existing catalysts operate too inefficiently for this, or they separate too much carbon.
- A large quantity of chemical impurities and metals needs to be removed under hydrogenation almost entirely from the products.
- In order to cover the increasing demand for paraffin hydrocarbons with a low degree of branching, methods need to be developed for hydrogenation and subsequent selective cracking of condensed aromatic compounds.

- The ever more stringent product specifications and the deteriorating quality of the crude oil are major hurdles for new catalytic methods to overcome.
- The key to the continued supply of raw materials from crude oil is tailor-made control of the molecular weight along with the introduction of hydrogen into heavier crude oils.

## 1.2. Natural gas

Natural gas deposits occur both in tandem with crude oil deposits as well as in pure natural gas fields. After any carbon dioxide, hydrogen sulfide and other inert gases which may be present have been removed and the gas has been dried, it comprises almost exclusively short-chain alkanes. Alongside methane (75 – 99 %), other important components of natural gas include higher alkanes, particularly ethane (1 – 15 %), propane (1 – 10 %) and butane (0 – 3 %). Associated natural gas from crude oil wells is frequently richer („wetter“) in terms of these higher alkanes than non-associated gas. As well as being transported in pipelines, natural gas is often liquefied for transportation: liquefied natural gas (LNG) is mostly made up of methane, while the higher alkanes are described as natural gas liquids (NGL); the propane/butane fraction of the NGL is traded under the name liquefied petroleum gas (LPG). The availability of methane via the known natural gas reserves could be significantly increased through the exploitation of methane hydrate deposits on the sea bed as well as through the production of biogas from renewable raw materials.

Natural gas is already used as a raw material in the chemical industry; primary applications include the use of ethane for ethane cracker and methane in synthesis gas

production. Whereas the ethylene production in ethane crackers is an uncatalyzed reaction, a heterogeneous catalyst is required in the standard methods currently employed for the production of synthesis gas (mixture of carbon monoxide and hydrogen) from methane and water steam („steam reforming“). Due to the high hydrogen content in the methane, the synthesis gas produced from natural gas has a high „natural“ hydrogen content, which at a ratio of hydrogen to carbon monoxide of 3:1 is higher than in production processes from other raw materials like crude oil, coal or biomass. With the aid of the water-gas shift reaction (WGS), in which carbon monoxide reacts with water vapor to form hydrogen and carbon dioxide, it is ultimately possible to arbitrarily adjust the hydrogen content of a synthesis gas. In addition, methane is also used in the chemical industry in the production of acetylene, methyl halogens and hydrogen cyanide. The Andrusow process for the production of hydrogen cyanide from methane, ammonia and oxygen is another example of a natural gas based process involving heterogeneous catalysis which is important today.

Of all of the fossil fuels, reserves of crude oil are due to run out first, so it is set to become significantly more expensive in the future. As a result, it is very likely that natural gas will become more important for the chemical industry in the future as it is a raw material which is easy to transport and handle. The most important chemical primary products made from crude oil are olefins (particularly ethylene and propylene) and aromatic hydrocarbons (particularly benzol, xylenes) which are produced using the steamcracking process and the reforming process. Consequently, the greatest future potential for natural gas in the chemical industry therefore lies in the production of precisely these primary products.

Whereas the long-chain hydrocarbons in the crude oil are separated into the required chemical products through the process of „cracking“, for the short-chain alkanes in the natural gas – and here in particular for the C<sub>1</sub> building block methane – it is the carbon linking reactions which play a decisive role. Examples of these exclusively heterogeneous catalysis reactions from the current research

- » With reduced availability of crude oil as a raw material for the chemical industry, natural gas will be elevated into a more prominent role.
- » New catalytic technologies for the production of – in particular – olefins and aromatic compounds or their direct secondary products from natural gas are needed.

landscape include the synthesis of aromatic compounds from methane or LPG (Cyclar process) and the production of ethylene from methane. This class also includes synthesis gas based techniques for producing olefins (e.g. methanol-to-olefins, MTO), alcohols and higher alkanes (gas-to-liquid, GTL, for fuels); here, techniques based on the Fischer Tropsch (FT) process will become even more important.

Alongside the process of cleaving the alkanes contained in the crude oil into products with the required chain length, the process of steamcracking which is used today fulfills another important task: olefins are produced from alkanes. This means that functionality is introduced in the form of double bonds – and without these, further refinement in chemical value chains is not possible. It is therefore foreseeable that alternative technologies for „activating“ alkanes will become more important with the increasing significance of natural gas. Examples of such technologies include on the one hand dehydrogenation processes, which are used to produce propylene from propane in a heterogeneous catalysis process, and the oxidation of alkanes with oxygen on the other. The latter process can for example enable the direct production of methanol or formaldehyde from methane, of ethanol or acetic acid from ethane, or of propanols or acrylic acid from propane.

The forecast reduction in the availability of crude oil as a raw material for the chemical industry will elevate natural gas into a more prominent role. This will make it necessary to develop new technologies which will enable in particular the production of olefins and aromatics or their direct secondary products from natural gas. Important research goals which can only be achieved with the aid of heterogeneous catalysis include:

- **Carbon linking reactions**
  - Aromatic compounds and olefins from methane
  - Synthesis gas based methods (e.g. methanol-to-olefins, Fischer Tropsch synthesis)
- **Alkane activation reactions**
  - Dehydrogenation processes
- **Alkane oxidation processes**
  - Partial oxidation (e.g. methanol from methane)

### 1.3. Coal

From the early days of the chemical industry right through to the middle of the 20th century, coal was the main source of raw materials, before it was then superseded by cheaper petrochemical starting materials. For some classes of materials, coal still remains an important raw material for the chemical industry, as for example many basic aromatic compounds – particularly multinuclear aromatic compounds – are almost entirely produced from coal tar.

In contrast to its rather insignificant reserves of crude oil and natural gas, Germany has large deposits of hard coal and lignite which are currently used to generate electricity as well as for the production of iron and steel. Unlike hard coal production, the German lignite industry is also internationally competitive.

Basically, the following three primary methods are available for the refinement of coal and for the production of fuels and bulk chemicals:

#### Hydrogenation (direct coal liquefaction)

In order to hydrogenate coal, grounded coal is suspended in coal-derived oil and converted into a liquid hydrocarbon mixture in the presence of a solid, transition metal based catalyst and hydrogen under high pressure at temperatures of around 450°C. One alternative is indirect hydrogenation, e.g. with tetralin. After separation of the residue via distillation, further processing of the obtained coal oil is required as it contains large quantities of aromatic compounds and S and N-compounds. This is done via the process of hydro-treating.

#### Gasification

Coal gasification is the first stage in the indirect coal liquefaction process. Here, the coal is converted with oxygen and water vapor into a CO-rich synthesis gas made up of CO and H<sub>2</sub>. Afterwards it needs to be purified (removal of dust, sulfur, nitrogen and other heteroatoms), before the correct CO:H<sub>2</sub> ratio required for subsequent processes is adjusted with the aid of the watergas shift reaction.

#### Degasification

During the process of coking black coal, volatile components are produced at high temperatures under the absence of air; in addition to coke oven gas, this also includes the coal tar which is separated and routed for further processing. This is the most important source of condensed aromatic compounds.

Further **need for research and development work** in the field of coal refinement is closely connected with catalysis and focuses primarily on the following priority topics:

#### Coal hydrogenation

- Replacement of current single-use catalysts with resistant, efficient and recyclable catalysts for liquid phase hydrogenation.
- Optimization of the catalysts for hydrotreating for further processing of the coal oil.
- Development of integrated process engineering concepts.

#### Coal gasification

- Development of sulfur resistant catalysts (“sour gas shift catalysts”) for use at optimum temperatures for the shift reaction.
- New catalysts and methods for using synthesis gas (see section 5.3.).

#### Coal degasification

- Development of catalytic methods for selective conversion of aromatics from the coal tar.

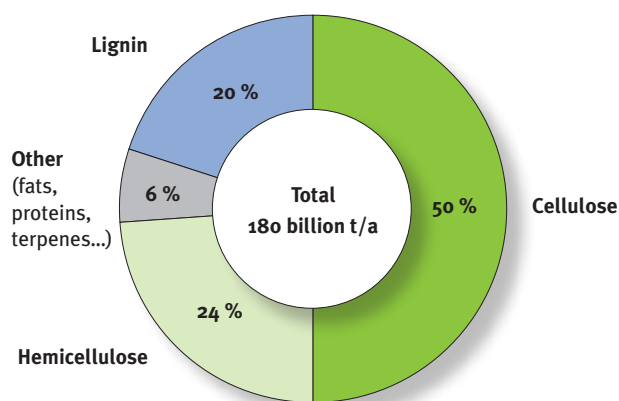
- » The refinement of coal for the production of fuels and bulk chemicals requires further investment in catalysis research.
- » New, innovative catalytic processes will enable even more efficient conversion of the coal via hydrogenation, gasification or degasification.

### 1.4. Renewable raw materials

Renewable raw materials in the form of terrestrial and marine biomass offer many different opportunities to sustainable material with added value. At present, renewable raw materials take a share of around 12 % in the consumption of raw materials in the chemical industry in Germany. Similarly to fossil carbon sources, there is also a close link to potential usage as an energy carrier. In addition, on account of direct or indirect competition between the production of biogenous raw materials and the production of foodstuffs, the importance of utilizing these resources in the most efficient possible way is paramount.

Against its international competitors in the field of catalytic conversion of renewable raw materials, Germany has an extremely competitive and increasingly well net-

worked research community across academic institutions and industry. This offers a highly promising starting position for one of the most important fields of innovation in the chemical industry and biotechnology for the future.

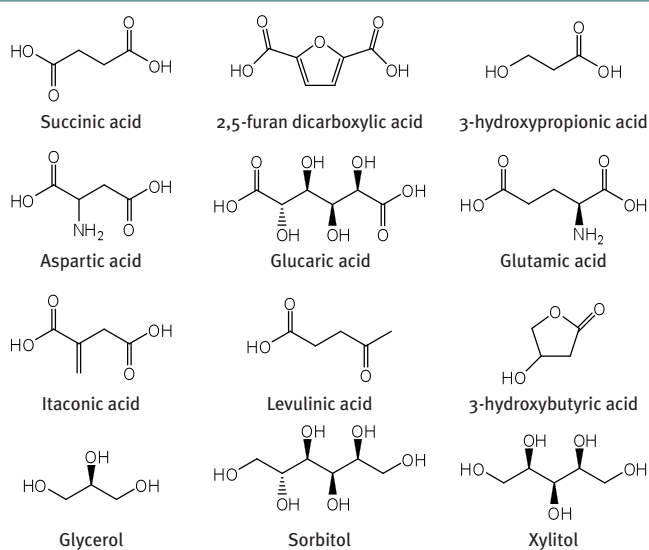


**Figure 2: Distribution of renewable raw materials across material groups (GDCh professional group for environmental chemistry and ecotoxicology)**

### Lignocellulose as a raw material

Lignocellulose is an extremely stable composite material made up of the three components cellulose (35-50 %), hemicellulose (25-30 %) and lignin (15-30 %). It forms the supporting material of all terrestrial plants, as a result of which both selectively cultivated bioenergy crops and waste streams can be exploited as sources of raw materials.

Starting from cellulose and hemicellulose, it is possible to generate family trees for the chemical reaction proc-



**Figure 3: List of the 12 potential biobased platform chemicals according to the US Department of Energy**

esses into chemical resources and materials. The study “Top Value Added Chemicals from Biomass” published by the US Department of Energy contains a list of 12 possible platform chemicals. Both the carefully managed production of these compounds from biopolymers and their efficient, selective and controlled further conversion represent an enormous challenge for fundamental research in the field of catalysis.

Lignin has a fundamentally different structure to the cellulose materials, featuring an elongated, irregular structure made up of aromatic building blocks which are linked via oxygen or carbon bridges. As a result, lignin could represent an important source of aromatic building blocks.

### Starch and sugar as raw materials

Glucose, molasses and starch already play a very important role today as raw materials for industrial biotechnology, which is also referred to as white biotechnology. In addition to the chemical/catalytic conversions from cellulose under removal of oxygen already mentioned for the carbohydrates, selective oxidation reactions of sugar and the derived platform chemicals are of great interest. Particularly the production of dicarboxylic acid (such as succinic acid) as building blocks for biodegradable polyesters and polyamides offers high potential for added value.

### Oils and fats as raw materials

Today, oleochemistry is already an important economic factor. In 2008, approximately 165 million tons of fats and oils were produced worldwide, and the corresponding amount in Germany was 2.5 million tons, of which around 9 % was processed into oleochemical products (soaps, detergents, paints/varnishes, hydraulic fluids/lubricants, biofuels, printing inks etc.). Catalytic innovations in oleochemistry offer the basis for further use of these raw materials.

Both the acid groups and in particular the double bonds in the fatty acid molecules offer wide potential for modification and material changes to raw materials from plant-based and animal-based fats and oils.

### Terpenes

Terpenes and resins are important by-products of the timber industry. They are made up of isoprene units, and just like the unsaturated fatty acids they contain usable functional groups in the form of C-C double bonds.

This applies both to selective oxidation processes and C-C linking reactions as well as to polymerization and copolymerization processes.



Research and development work in the field of material usage of renewable raw materials needs to be carried out in the following areas in particular:

- **Decomposition and depolymerization of cellulose:**  
Unlike sugar or starch, in its native form cellulose is extremely difficult to access and comparatively resistant to cleavage into oligomer or monomer carbohydrate units. New chemical catalytic and biocatalytic processes, including those involving innovative solvent concepts (see section 6.3.) can open up new approaches.
- **Decomposition and depolymerization of lignin:**  
The production of defined starting substances through the decomposition of lignin represents a major challenge, with similar issues needing to be addressed as for cellulose.
- **De/refunctionalization of the biogenous raw materials:**  
While the petrochemical value chain is based on the principle of the increasing establishment of functional groups in hydrocarbons, cellulose and carbohydrates are “over-functionalized” as raw materials, i.e. they contain too many reactive groups. The conversion of the material must thus concentrate not only on the formation of, but also on the selective reaction or decomposition of such units, for which new catalysts and processes will need to be found and developed.
- **Development of water-stable catalysts / carrier materials:**  
Within the process of the conversion of biogenous raw materials, it is increasingly necessary to carry out catalytic processes in the aqueous phase. This places increased demands on the stability of the catalysts and/or the catalyst carriers, and makes it necessary to develop catalysts and catalyst carriers which are stable in water.
- **Integration of the reaction and material separation**  
(See section 6):  
As biogenous raw materials are highly polar substances with low volatility, the chemical reactions need to be performed primarily in solution. This demands new concepts for the integration of the reaction and material separation, which in turn will allow the energy and material balances to be improved.
- **The concept of biorefinery**  
Similarly to crude oil, a wide range of different material flows are generated when biogenous raw materi-

als are processed for use as materials. For industrial-scale implementation of new processes on the basis of renewable raw materials, it is essential that a large proportion of the biogenous starting materials is converted into usable end products and does not remain unused as a waste stream. Consequently, in addition to the development of efficient solutions for individual reaction steps, it is also important to have an overall concept in which sufficient value is created in the individual process streams.

- » Against its international competitors in the field of the catalytic conversion of renewable raw materials, Germany has a very promising starting position across academic institutions and industry.
- » Innovative value chains on the basis of carbohydrates instead of hydrocarbons.
- » Defunctionalization instead of functionalization as the synthesis strategy.
- » Development of new concepts for integration of the reaction and separation of materials for energy-efficient processes.

## 1.5. CO<sub>2</sub> usage

The use of CO<sub>2</sub> – which is available in large quantities and in concentrated form as a waste product from the energy industry or from other sources – as a material represents an attractive contribution to an overall carbon management strategy both from an environmental and commercial point of view if a non-fossil energy source is available. Here, only a limited direct contribution to the reduction of CO<sub>2</sub> emissions is possible, as is highlighted by a comparison of the current anthropogenic emissions of carbon dioxide of around 29 Gt/a to the estimated global substitution potential of around 180 Mt of CO<sub>2</sub> in chemical products.<sup>3)</sup>

Due to the specific thermodynamic and kinetic boundary conditions, interdisciplinary cooperation is required between chemical engineers (basic principles of molecular chemistry, new catalysts) and process engineers (energy balances, process intensification) particularly in the area of carbon dioxide exploitation.

Based on the underlying chemical reactions, the following main areas of focus can be identified:

The **hydrogenation of CO<sub>2</sub>** leads to important chemical products like methanol or formic acid and their derivatives. Many promising catalyst systems have already been

<sup>3)</sup> Discussion paper „Use and Storage of CO<sub>2</sub>“, DECHEMA, October 2008

identified for these reactions, which are usually exothermic. To date, processes for hydrogenation into longer-chain alcohols or polyols have been little researched. However, as hydrogen is currently produced almost exclusively from fossil fuels, a direct reduction of CO<sub>2</sub> emissions cannot be achieved until CO<sub>2</sub> is hydrogenated with H<sub>2</sub> from regenerative sources (see section 2.2.).

Through the process of dry reforming it is possible to convert CO<sub>2</sub> into carbon monoxide (CO) (e.g. with methane into synthesis gas, or with benzol into phenol and CO), which can be used similarly to the CO from other sources for chemical synthesis processes. Despite the additional energy requirements, this type of concept may be interesting under specific conditions.

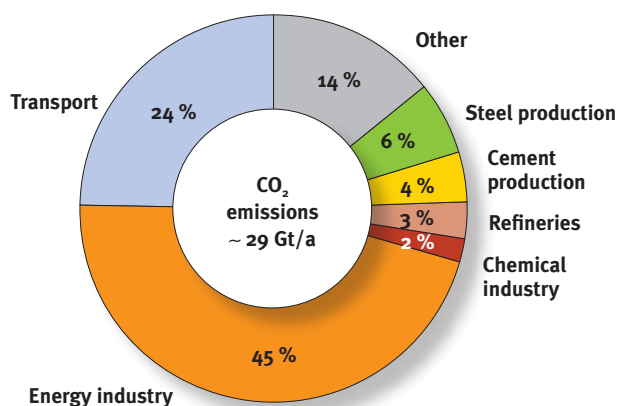


Figure 4: CO<sub>2</sub> sources and emissions resulting from the use of fossil fuels (source: Discussion paper „Use and Storage of CO<sub>2</sub>“, DECHEMA, October 2008)

The formation of **carbonates and polycarbonates** from CO<sub>2</sub> offers direct access to extensive markets in the chemicals and plastics sectors. Recently, significant progress has been made in the area of catalysis research both in academic institutions and in the industry. Special plastics have just been launched to market in the USA which are produced via copolymerization with CO<sub>2</sub>. For Germany as a country with leading industrial companies in the areas of polycarbonates and polyurethanes, this approach offers major innovation potential for application-oriented fundamental research.

Electrocatalytic and – in particular – photocatalytic reduction of CO<sub>2</sub> would represent another very elegant form of use for carbon dioxide modeled on the synthesizing power of nature in the process of photosynthesis. However, the heterogeneous and homogeneous catalyst systems known today still require significant improvements before technical efficiency levels are reached which can be commercially exploited.

A number of active catalysts are available for coupling carbon dioxide with unsaturated substrates like butadiene or acetylenes. However, with the exception of certain telomerization reactions (Kuraray process), no market exists for the products generated in the process, so further technological development will have to incorporate both the manufacturing process and the development of products.

The direct carboxylation of hydrocarbons through formal insertion of CO<sub>2</sub> into the C-H bond of alkanes, aromatic compounds or olefins is one of the “dream reactions” of modern catalysis research. As a general rule, these reactions are thermodynamically impossible. There are a few exceptions to this, including the conversion of methane and CO<sub>2</sub> into acetic acid, benzol and CO<sub>2</sub> to benzoic acid, and ethylene and CO<sub>2</sub> to acrylic acid. Even though fundamental research into organometallic chemistry could deliver important insight into potential catalytic cycles, no efficient solutions are currently available for this problem.

The innovation potential for use of CO<sub>2</sub> as a material thus lies predominantly in the following areas:

- » The use of carbon dioxide as a material opens up new opportunities for creating value on the basis of a waste product from the energy industry.
- » A range of reactions exists in which CO<sub>2</sub> remains in the end product as an inexpensively available and ecologically advantageous C<sub>1</sub> building block in the end product.
- » Contributions towards direct reductions of carbon dioxide emissions are limited in terms of the use of CO<sub>2</sub> as a material.
- » Photocatalytic or electrocatalytic activation of CO<sub>2</sub> is modeled on natural processes.

- Photocatalytic or electrocatalytic activation modeled on natural processes.
- Synthesis of products with high added value, in which CO<sub>2</sub> remains in the product as a C<sub>1</sub> building block.
- Hydrogenation of CO<sub>2</sub> with hydrogen from regenerative sources.

## 2. Securing energy supplies

As was already discussed in chapter 1, securing energy supplies is closely tied in with securing the supply of raw materials, and as a result these two issues cannot be treated in isolation.



### 2.1. Fuels of the future

Even though the importance of hydrogen and stored chemical energy (batteries) as energy carriers is set to rise significantly, it can be expected that the bulk of fuels for mobile applications will continue to be based on hydrocarbons. While demand in developed industrial nations will either stagnate at a high level or possibly even drop slightly, overall there will be a huge global increase in the quantities of fuel which are required. The proportion of compounds containing oxygen in the fuel pool will increase slightly, as on the one hand biogenous carbon sources are being developed and on the other hand a certain concentration of oxygen in the fuel has a positive effect in terms of combustion properties. Alongside conventional fuels from fossil sources, there will be regionally varying proportions of biogenous fuels based on renewable raw materials:

- Biodiesel from fatty acid methyl esters and their hydrogenated derivatives
- Ethanol from alcoholic fermentation

As the availability of types of crude oil which are easy to process will be reduced at the same time, it will become increasingly necessary to work with heavy types of crude

oil, oil sand and oil shale. These are rich in heteroatoms (sulfur, nitrogen, phosphorus) and metals. In order to satisfy the quality and environmental requirements placed on modern fuels, sulfur and nitrogen concentrations in the products must be restricted to maximum levels of 10 ppm, and the octane rating and cetane number of the products must be easy to adjust. Other general objectives include a reduction of the vapor pressure, the minimization of aromatic compounds (toxicity), naphthenes (poor octane rating) and olefins (stability).

Fuels which satisfy these requirements should be made up of hydrocarbons of varying size with different degrees of branching and an H/C ratio of 2 in order to minimize the CO<sub>2</sub> emissions at any given engine output. However, as the starting products contain a significantly lower hydrogen-to-carbon ratio, either hydrogen needs to be added or carbon needs to be removed. Provided the hydrogen required for this purpose is produced from fossil sources then the first route will always lead to a significant increase in CO<sub>2</sub> production, and the second route will do so in many cases. This can only be minimized if the hydrogen is produced from renewable resources or the CO<sub>2</sub> which is generated in the process is separated and sequestered. The key steps in this process are listed below in the form of bullet points.

## New processes and catalysts for fuels

- Production of synthesis gas from methane, coal or biogenous sources with subsequent GTL (“gas to liquids”) processes via two principal routes: (a) synthesis of methanol and its conversion to dimethylether, C<sub>2</sub> and C<sub>3</sub> olefins as well as of gasoline, plus (b) Fischer Tropsch synthesis with subsequent conversion of the products via hydro-isomerization and hydrocracking as well as oligomerization of olefins.
- New catalysts for direct conversion of methane into higher hydrocarbons. New catalysts for conversion of synthesis gas to ethanol and higher alcohols.

## Improved conventional processes and catalysts for fuels

- Reduction of sulfur and nitrogen in heavy crude oil fractions.
- Enable high variability of starting materials like vacuum gas oils, vacuum residues and admixing of bio-oils, plastic waste, oil shale extracts and oil sand extracts in refinery processes.
- Alternative solid catalysts for alkylation of C<sub>3</sub>-C<sub>5</sub> alkenes with isoalkanes.
- New catalysts and processes for selective catalytic cracking of naphtha in propene and ethylene.

- » Future fuels will be increasingly based on C<sub>1</sub> molecules, for which it is necessary to develop new catalyst systems and processes which incorporate renewable energy and starting materials.
- » In conventional processes, increasing use is being made of starting materials which have a low hydrogen content and which are contaminated with heteroatoms. New catalysts need to be capable of converting these molecules into a conventional range of products.
- » One of the key problems is to find efficient ways to bring in sustainably produced hydrogen.

## 2.2. Hydrogen production and storage

Hydrogen is one of the most important environmentally safe energy carriers of the future. It can be produced from numerous raw materials and used efficiently as a source of energy in stationary, decentralized and mobile applications. However, the qualification of hydrogen as an energy carrier requires further efforts in the field of cost-effective and safe provision, storage, distribution and conversion.

State-of-the-art processes include steam reforming and/or the partial oxidation of natural gas or other fossil carbon sources. From the synthesis gas which is produced, ultra-pure hydrogen is then obtained in a several-stage process (watergas shift reaction, selective oxidation or selective methanation). The process chain is also suitable for decentralized production of hydrogen under non-stationary conditions and is thus a key element for a widespread hydrogen infrastructure which offers full coverage across the market area. For such dynamic boundary conditions, the service life of the catalysts involved would need to be improved and the activity and selectivity of the purification methods would need to be increased. In view of the foreseeable shortage of fossil hydrocarbon sources, new ways to get at hydrogen will need to be found and developed to technical maturity before the transition to hydrogen as an energy carrier can be made.

The production from biomass or waste materials of synthesis gases containing hydrogen via the modification of classic reformation behavior thus suggests itself as an obvious route. Here, the variable composition of the raw materials represents a particular challenge in terms of the robustness of the catalysts.

The process of electrolytic cleavage of water is technically already possible. Energy efficiency is quoted as being around 70 %, although this only applies to stationary operation, which is not always the case when using regenerative energy sources. Optimized processes need to be found for such operating conditions. Today, nickel is used predominantly as the catalyst; platinum would be better in terms of energy efficiency but is too expensive. Cheaper electrode materials with a similarly low overvoltage to platinum could help to bring about significant progress here. In addition, it is also important to test and optimize new process variants, such as high-pressure electrolysis or gas phase electrolysis.

Photocatalytic water cleavage processes are still a long way off commercially viable space-time yields, regardless of whether they are based on solid catalysts or biochemi-

cal/biomimetic systems. The situation is similar for the (to date) undervalued alternatives of homogeneous or biocatalytic methods. In the area of biocatalysis, past work has focused particularly on discovering the fundamental biochemical principles and regulatory processes for microorganisms which can be used to produce hydrogen or fix nitrogen. As in all cases these enzymes carry a complex metal cofactor in their active center and also display a pronounced oxygen intolerance, to date they have been used only rarely in biotechnology applications. Finally, some initial progress has been made with approaches to produce hydrogen in electrochemical cells by converting CO<sub>2</sub> into synthesis gas. All of these techniques are still in an early stage of fundamental research, but they all have the potential to revolutionize hydrogen production in the long term.

For mobile applications, as an alternative to on-board production hydrogen can also be stored in suitable tanks which are carried on the vehicles. Here, high-pressure storage (up to 700 bar) and cryogenic storage of liquid are being demonstrated and evaluated in some initial projects. Hydrogen-adsorbent materials and/or hydride-forming solids promise improved **volumetric** storage densities at lower pressures and moderate temperatures. For example, hydrogen can now be reversibly adsorbed at -200 °C on activated charcoal and MOF materials at a rate of up to 7 mass percent. The development of adsorption materials with very large specific surface areas and adsorption capacities at room temperature including the associated inexpensive synthesis routes is another important task for the future. With regard to sufficient **gravimetric** storage density, only light metal hydrides offer a viable alternative. Here, compounds need to be identified which offer a lower enthalpy of formation and which enable faster charging and discharging processes in combination with catalysts.

The research requirements in the field of hydrogen can be summarized as follows:

- Provision of sufficient active and stable catalyst systems for the reformation of hydrocarbons in decentralized systems.
- Provision of highly active and selective catalysts for the purification of synthesis gas.
- Decentralized, climate-neutral hydrogen production from cultivated biomass or from the exploitation of secondary materials via autothermic reformation.

- Improvement of water electrolysis processes, both in terms of the electrocatalysts and in terms of process control.
- Long-term research projects looking into photocatalytic water cleavage with new catalyst systems in order to create a simple way to supply the hydrogen required for the hydrogen industry.
- Synthesis routes for inexpensive adsorbent materials with a high H<sub>2</sub> storage capacity.
- Light metal hydride storage solutions which are suitable for practical applications and which, thanks to suitable catalysts, offer a sufficiently dynamic kinetic for use in fuel cells.

- » Hydrogen is one of the most important environmentally safe energy carriers of the future.
- » However, in view of the foreseeable shortage of hydrocarbon sources, new ways to get at hydrogen will need to be found and developed to technical maturity, whereby the variable composition of the raw materials represents a particular challenge in terms of the robustness of the catalysts.
- » Research in the field of photocatalytic cleavage of water has a great strategic importance in terms of establishing a new hydrogen system.

### 2.3 Fuel cell technology

Fuel cell technology is a technology for converting energy which offers significantly higher efficiency than conventional energy conversion processes. Thermodynamically, efficiencies above 65 % are possible. However, the degrees of efficiency achieved in practice are between 35-45 %. In applications where it is possible to use the heat which is released during the process (combined heat and power plants in stationary applications) a total efficiency of more than 80 % can be achieved.

The use of fuel cells always results in a significant lowering of harmful gas emissions (NO<sub>x</sub>, CO, hydrocarbons). However, in any assessment of a reduction potential in climate-relevant CO<sub>2</sub> emissions the H<sub>2</sub> production process also needs to be taken into account. Here, the complete energy conversion chain including centralized H<sub>2</sub> production from fossil fuels with its conversion, transport and storage losses results in only slightly better numbers compared to direct use of the hydrocarbons in internal

combustion engines. However, if hydrogen from “green” sources like biomass, biogas or wind power is used, then the fuel cell – as a fitting, highly-efficient conversion technology – is the missing link in the non-fossil energy cycle of the future.

The impact of the different types of fuel cells depends on the fields in which they are used. They can be classified in the following three categories: stationary applications (SOFC, MCFC, PEMFC), portable applications (primarily DMFC, but also PEMFC) and mobile applications (PEMFC).

In the following, we take a brief look at each of the most important types of fuel cell and discuss some of the current challenges they face from a catalysis point of view.

Particularly high expectations are placed on **proton exchange membrane fuel cells (PEMFC)**, which have been developed to quite an advanced stage for a number of different applications. To date, PEMFCs are operated at temperatures between 70-80°C. Both the anode and cathode reactions of the PEMFCs require catalysts from the platinum metals group.

The hydrogen PEM fuel cell (H<sub>2</sub> PEMFC) is the technology which is foreseen for use in automotive applications. According to announcements made by automotive manufacturers, first close-to-production vehicles are set to be available for end customers from 2015, and higher volumes are planned from 2020 onward. For automotive applications, the necessary load change stability and start-stop-cycle stability represent the most challenging demands, along with the target costs per kW output power. With the catalysts developed so far on the basis of platinum or platinum alloy nanoparticles on carbon supports with a large surface area, the costs per kW of output power (largely the costs of the precious metal which is used) is still around twice the value which would be viable for a commercial launch. Long-term stability is another issue which is still unsatisfactory. In addition, future developments will be aimed at increasing the operating temperature of the PEMFC to as much as 120°C. The main requirement for this is the development of membranes which show a low resistance even under significantly reduced humidification. At the same time, the increase in operating temperature also represents a further challenge for the stability of the catalyst.

**Solid oxide fuel cells (SOFC)** have been primarily developed for stationary applications; due to the high operating temperature (800°C) the particular challenge here is to ensure thermal cyclability. Nickel catalysts are used pri-

marily, with the aid of which both methane and CO can be used as the anode fuel gas. Increasingly, the use of SOFCs is also gaining importance for smaller power output classes as auxiliary power units (APU). A pre-reforming stage is sufficient in order to provide the suitable fuel gas for the fuel cell. This significantly reduces the complexity of the system in comparison to PEMFC systems, and takes us closer to the introduction of fuel cell systems for logistically available fuels. The targeted output power is in the range of 1 kW for leisure applications and up to 5 kW for transport applications.

The **molten carbonate fuel cell (MCFC)** is a further high-temperature fuel cell. A melt of potassium and lithium carbonate acts as the electrolyte at 600-650°C. As a result of the high operating temperatures, the MCFC is tolerant to carbon monoxide (CO) and is particularly well suited to fuel gases with a higher carbon content. A desulfurization stage and a pre-reforming stage are sufficient for fuel gas conditioning. The main challenges here are to increase service life by optimizing the corrosion resistance of the individual materials and to reduce costs. Potential areas of application for MCFCs include e.g. industrial heat and power coupling systems and stationary power production in the medium and high power output ranges.

The power densities currently achieved with the **direct methanol fuel cell (DMFC)** are around 10 times below those achieved with H<sub>2</sub> PEM fuel cells. The main difficulties here are – on the material side – the anode activity, which is far too low, and the too high crossover of methanol to the cathode where it causes losses in voltage potential; as a result, it is necessary to work with lower water/methanol ratios in practice. Another task which is of general importance is the miniaturization of the fuel cell and its peripheral components for use in portable devices. For this, special structures need to be developed which allow passive operation, i.e. without the support of auxiliary units. Current devices for portable applications are delivering power in the range of 100 mW. Systems for charging stations and energy supply systems for on-board electronics in caravans and on yachts are currently delivering in the region of 50-100 W.

The following development lines have a strategic importance in the field of fuel cells:

#### 1. PEMFC:

- Development of load change and cycle resistant electrocatalysts for automotive PEMFCs in an operating range from -40°C to + 120°C with
  - an electrochemical activity which corresponds to a platinum mass activity of  $\geq 0.4$  A/mg Pt;
  - an electrochemical voltage potential stability of the catalyst of more than 300,000 load change cycles and 30,000 start-stop-cycles.
- Development of non-precious metal electrocatalysts.

#### 2. DMFC:

- Development of new DMFC anode catalysts and anode structures with significantly lower anode overvoltages and higher voltage potential stability.
- Development of innovative cathode catalysts for DMFC which are insensitive to methanol.
- Development of special electrode micro and nano structures for passive and vapor driven DMFCs (micro fuel cells).

#### 3. SOFC:

- Anode catalysts with long-term stability and significantly reduced tendency towards carbon formation for conversion of higher hydrocarbons in SOFC.

- » In cases where they are operated with regeneratively produced hydrogen, fuel cells make an important contribution towards the minimization of harmful gas emissions.
- » The requirements placed on the catalysts for fuel cell systems depend on the type of the fuel cell used and comprise, among other things, activity, long-term stability and cost reduction.

## 2.4. Electrocatalysis

Electrochemical process engineering is currently largely dominated by the production of the basic chemicals chlorine and sodium hydroxide within the framework of chloralkali electrolysis. In this area – which is also referred to as electrocatalysis – major progress has been made in recent years with regard to energy savings and hence reduced CO<sub>2</sub> emissions. For example, by combining fuel cell technology (specifically the alkaline fuel cell) with a conventional electrolysis cell, it has been possible to lower the cell voltage required for operation of such systems by nearly one Volt. No hydrogen is produced in this process; instead, the supplied oxygen is “consumed” and converted into hydroxide ions. This technology is also referred to as oxygen consumption cathode technology (SVK).

Approximately 5 % of worldwide chlorine production is carried out with the aid of hydrochloric acid electrolysis; 240 kt of chlorine per year is currently produced using the hydrochloric acid/SVK technology. SVK technology has already been developed for this electrolysis on the basis of technology components of the proton exchange membrane fuel cell (PEM). The transfer of PEM fuel cell expertise to hydrochloric acid electrolysis was made possible by major advances in the area of the development of electrocatalysts on the basis of rhodium sulfide. More research particularly in the area of the electrocatalyst will hopefully result in a further lowering of the necessary cell voltage and therefore a reduction of the energy requirements.

Electro-organic synthesis processes have not been able to establish themselves on a larger scale apart from the process for the production of adipodinitrile (Monsanto/Baizer process). Once again, the key to this process is the right choice of electrocatalyst. This process currently still has an annual capacity of approximately 500,000 t. In addition, the process of electrofluorination is also known and used on a reasonably large scale (Simons process and Phillips process). These processes are used to trigger the perfluorination of organic substances in hydrogen fluoride or in KF/HF.

Particularly in Asia, intensive research is still under way to investigate new electrode materials and electrocatalysts. In Europe, conductive (boron-doped) diamond electrodes for aromatic linking reactions were recently discussed; these are intended among other things for the synthesis of fine chemicals with greater added value.

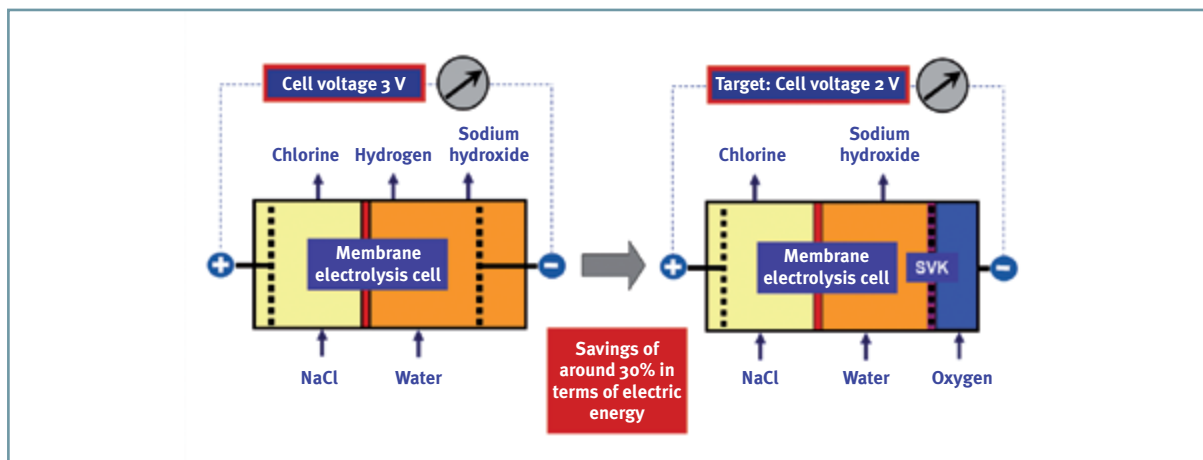


Figure 5: Chloralkali electrolysis: Comparison of a conventional electrolysis cell (left) with the oxygen consumption cathode technology (SVK) (right-hand side)

Further need for research:

- Improved electrocatalysts which will lower the necessary cell voltage even further and thus lead to lower energy consumption.
- Improved and more stable membranes for the electrochemical cell structure.
- Transfer to other methods in the primary industry.

- » Improved understanding and new electrocatalysts can lead to significant energy savings.
- » New electrodes will open up access to new reactions in fine chemistry.



## 3. Health and nutrition



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### 3.1. Active ingredients

The development of new active ingredients in the fields of pharmaceuticals and agriculture plays a significant role in terms of feeding and providing healthcare for an ever growing world population. For example, the problems associated with increasing occurrences of bacterial resistance to existing antibiotics can only be solved with the aid of new active pharmaceutical ingredients. Due to the stereoselective nature of interactions between active ingredients and the target, there is an increasing demand for enantiomerically pure compounds. In the process, it is possible for the two enantiomers of an active ingredient to have a different efficacy, and in addition they can also cause different levels of side effects. Against this background it is understandable that, for example in 2004, of the ten best-selling pharmaceuticals more than half were offered in an enantiomerically pure form – and this proportion is set to rise in response to legislative requirements. This increase in demand for enantiomerically pure compounds is accompanied by huge academic advances in the field of asymmetric synthesis and catalysis, although in many cases these cannot yet be translated into industrial practice.

Of the various different ways to produce enantiomerically pure active ingredients, asymmetric catalysis is often the

most advantageous process in terms of its ecological impact. Here, the chiral resolution process (i.e. non-selective synthesis of the enantiomeric mixture and subsequent separation), which results in the loss of 50 % of the material, is still the most commonly applied method for the production of active ingredients. The challenge is to develop techniques for dynamic chiral resolution, in which the enantiomer which is not used is re-racemized. This is usually done through a combination of different catalytic steps.

In the field of academic research, asymmetric homogeneous methods and biocatalytic methods currently dominate. However, only few of these methods are applied in the industry, e.g. asymmetric catalytic hydrogenation processes and biocatalytic kinetic chiral resolution processes, as the majority of the known asymmetric catalysis reactions are not up to the required industrial and hence commercial standards. Further important issues requiring improvement include the reliability of these processes and the frequent need for complex (catalyst) optimization, as swift realization is hugely important for commercial success. The development of robust and predictably successful catalyst systems on the basis of a quantitative understanding of the processes taking place would thus represent an important breakthrough. At least to some extent this has already been realized in the area of bioca-

talysis, where metabolic pathways of bacteria are being altered accordingly on the basis of material flow analyses.

Catalytic reactions used in the fields of bulk and fine chemicals are applied to modify known pharmaceuticals lead structures of active ingredients. Organometallic catalyzed C-C coupling and selective oxidation reactions should be mentioned here in particular. It is anticipated that the increased use of catalysts will, on the one hand, have a positive effect on the production of active ingredients, while on the other hand it will also help with the process of finding new active ingredients. The following development lines are particularly important in the field of chiral active ingredients:

- Development of highly selective and active catalysts which enable cost-effective production of enantiomerically pure compounds.
- Development of innovative biomimetic catalysts for asymmetric catalysis.
- Development of generally applicable chiral (bio-)catalysts for asymmetric oxidation and carbonylation reactions.
- Development of catalysts for enantioselective reductive amination processes.
- Development of new methods for dynamic racemic resolution.
- Mechanistic investigation and subsequent development of robust and predictably successful asymmetric catalyst systems.

In addition to the pharmaceutical active ingredients, which belong more in the field of medicine, there are also numerous compounds which play an important role in e.g. the cosmetics industry or other branches of industry due to their specific properties. These are covered in section 5.4. among others.

- » Biocatalysis and chemocatalysis play an important role for enantiomerically pure active ingredients.
- » In order to widen the scope of potential applications, better mechanistic understanding followed by the development of predictable catalyst systems are required.

## 3.2. Human food products and animal feed

The growing world population generates an increasing demand for protein, which can be provided either by selectively increasing the animal population or by intensifying the use of plant-based sources of protein.

For selective and carefully managed refinement and finishing of natural human foodstuffs and animal feed sources, certain supplementary ingredients can be added to them in order to enhance their nutritional value or for other dietary reasons. Besides substances which improve the consistency and handling properties of the food, this particularly includes amino acids and vitamins in quantities based on a calculated demand, followed by minerals and trace elements.

With the production of foods for human consumption, various catalytic steps are used particularly during the actual production process, and these are dominated by enzyme catalysis. Examples include the use of proteases in cheese production or pectinases and amylases in the clarification and fining of fruit juices. Additives are also often produced with the aid of catalytic sub-steps. The sweetener aspartame is a dipeptide; biocatalysts are used both in the production of its building blocks and during their linking. However, conventional processes like catalytic hydrogenation are also still used, for example in the hardening of fats.

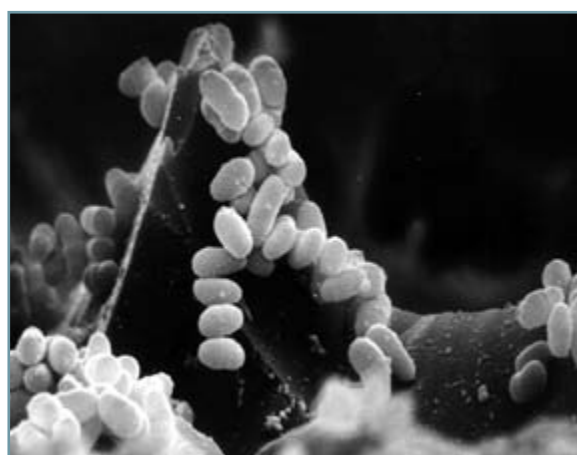


Figure 6: *Corynebacterium* for the production of amino acids  
(Source: FZ Jülich)

Modern livestock breeding techniques increasingly demand that more consideration is given to ecological factors, forcing the sector more and more into a demand-driven supply setup with high quality products from the mixed feed industry, particularly in situations where

nutrient-poor processed products from the agricultural industry are used like coarse colza meal, coarse soybean meal, wheat bran or whey.

The most important amino acids used in animal feed include in particular DL-methionine, L-lysine as HCl salt or sulfate salt, as well as L-threonine and L-tryptophan. Nearly 2 million tons of these protein building blocks are produced worldwide every year.

Without exception, all of the technical processes for industrial production of DL-methionine start from the same raw materials acrolein, methyl mercaptan, hydrogen cyanide or sodium cyanide – and large-scale production of these ingredients would be inconceivable without the use of highly efficient, heterogeneous catalysts. In addition, catalytic steps also play an important role during subsequent conversion of these substances in the methionine process. The equally important amino acids L-lysine, L-threonine and L-tryptophan are usually produced in a fermentation process from various carbohydrate sources, whereby a large number of enzyme catalytic sub-steps take place in the microorganism within the fermentation process.

The vitamins which are most important from a quantitative point of view and which are required as additives both for animal feed as well as for human foodstuffs are the water-soluble vitamins B1, B2, B5 and B6, and the fat-soluble vitamin E. Chemical and biotechnological manufacturing processes dominate here, along with combined processes. Vitamin E, which belongs to the chromanol family, is made up of a hydroquinone unit and an isoprenoid side chain, and in the process it is synthesized from small molecular building blocks in a series of acid or alkaline catalyzed condensation reactions and, in some cases, metal catalyzed steps which vary from one manufacturer to another.

For the production of additives, cost considerations thus lead to the following priority areas for strategic development:

- Reducing the number of steps in the synthesis process by using innovative catalysts in order to simplify the process engineering of the production process.
- Consistent introduction of catalytic synthesis steps instead of non-catalytic conversion steps in order to improve the commercial and environmental performance figures of currently employed chemical processes.

- In the case of methionine: optimization of the chemical and physical properties of the catalysts which are used with regard to a further increase in production yield and catalyst durability.
- Efficient production of amino acids and vitamins using biotechnological methods.

- The efficient production of additives like amino acids and vitamins depends to a significant degree on the development and use of innovative catalytic processes.
- Modern livestock breeding techniques increasingly demand that more consideration is given to ecological factors; they are forcing the sector into a demand-driven supply setup with high quality products from the mixed feed industry.

### 3.3. Fertilizers

The global fertilizer market plays an exceptionally important role, as around half of all humans live on food which is produced with the aid of fertilizers. Key components of modern fertilizers are manufactured using catalytic processes. Ammonia (NH<sub>3</sub>) is the key basic ingredient in the production of fertilizers containing nitrogen. More than 85 % of global ammonia production is used for the production of fertilizers. From the current annual growth in human population of around 1.2 %<sup>4)</sup> it is also clear that it will be necessary to increase fertilizer production. In 2006, the global market for inorganic fertilizers amounted to around 110 million tons of nitrogen (N) and around 130 million tons of ammonia<sup>5)</sup>.

A large number of catalysts are needed for the production of the starting materials hydrogen and nitrogen, as well as for the ammonia synthesis itself. The energy demands of the ammonia synthesis process are very large: Around 1 % of all the energy generated worldwide is required for the production of the hydrogen which is needed for this, which makes the production of ammonia the single biggest energy consumer in the world. Although the catalysts have already reached an advanced level of development, innovations will become interesting if they are able to deliver further improvements in terms of energy requirements and therefore in terms of the cost-effectiveness of the processes. As the production volumes are very large, even small improvements already have a major economic impact. A comparison of the individual components in ammonia plants shows that the section in which the natural

<sup>4)</sup> <http://esa.un.org/unpp>

<sup>5)</sup> CEH, Ammonia, 2007

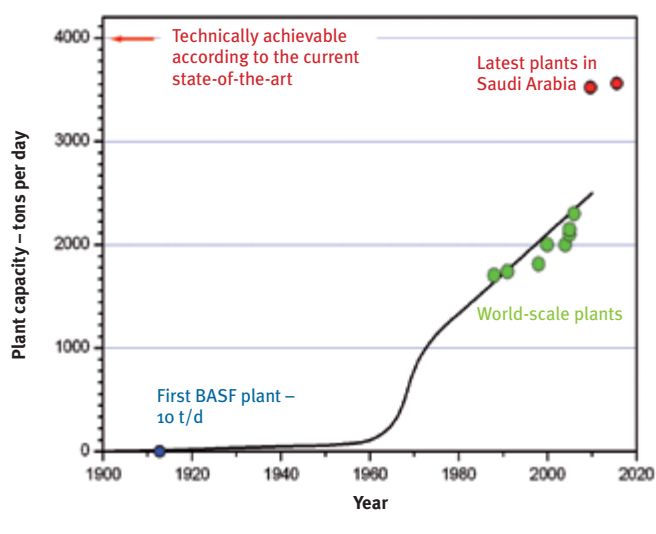


Figure 7: Production capacity of ammonia plants

gas is converted into synthesis gas (the “reformer”) accounts for a significant part of both the investment costs and the energy consumption.

Economies of scale mean that the greater the capacity of the plant is, the lower the investment costs are in relation to the quantity of ammonia which is produced. This has led to a continuous rise in plant capacity. Plants are cur-

- » Economies of scale demand ever larger plants in which the reactor and catalyst are perfectly matched to each other.
- » Due to the vast quantities which are produced, even small improvements to the catalyst and the resulting increases in terms of the yield or the selectivity of the reaction will lead to significant energy savings and represent a major reduction in the environmental burden.

rently running in Saudi Arabia with an output of 3,300 t/day. From a technical point of view, plants with a capacity of 4,000 t/day are feasible. Here again it is necessary to use highly efficient catalysts in order to keep the size of the reactors down to a minimum.

Totally new catalyst concepts are also conceivable which would permit direct nitrogen fixing at standard pressure and room temperature. However, these concepts have not yet been realized even at a laboratory scale with a sufficiently high yield.

The key developments which are of strategic importance for the production of fertilizers are as follows:

- The realization of very large ammonia plants requires the development of catalysts and apparatus which are carefully matched to each other.
- Ammonia synthesis with catalyst systems which for example mimic the active center of nitrogenase and permit a reaction at standard pressure and room temperature.
- Predictions of catalyst compositions with an improved efficiency for the fixing of nitrogen on the basis of physical and chemical surface properties.

## 4. Protection of the environment



### 4.1. Catalytic water and waste water purification

Water is not only the most important food we consume, but it also represents an essential ingredient without which agriculture cannot supply other foodstuffs for human consumption. Due to the increase in global population and improved standards of living, demands for clean water are set to rise dramatically in the future, and this will ultimately result in a massive shortage. Consequently, the protection of water as a vital resource is of fundamental importance to the existence of humanity.

In Germany, around 70 % of drinking water supplies are produced from groundwater. Already today, numerous surface waters and groundwater reservoirs are polluted with a large number of man-made substances, such as pesticides and their metabolites, halogenated or halogen-free hydrocarbons like methyl tert-butyl ether (MTBE), nitrate as well as pharmacologically or endocrine-active substances. This situation is likely to become worse in the next years and decades.

In addition to intensive farming, these problems are also caused by communal and industrial wastewater treatment processes which are not effective enough. Current water and wastewater treatment technology must be improved in order to meet the increasing demands of the future. The

supply of safe drinking water – itself a key basis for living – is inadequate or acutely at risk in many countries. Consequently, there is a demand for new, innovative technologies for water and wastewater purification. A distinction needs to be made here between the purification of industrial water on the one hand, which is discharged in a discontinuous flow but which is highly contaminated with complex pollutants, and the diffuse discharge of large volumes of water across polluted areas on the other.

In the sense of sustainable development and careful management of resources, we should initially turn to simple methods based on natural processes which biologically break down pollutants, such as root zone systems. If this type of system is unable to deal with the problem, then we can start to employ the usually more cost-intensive physical and chemical methods, which are usually also combined with microbiological methods.

One aim should be to transfer the great successes achieved with catalysis in the purification of gases to the purification of water, i.e. to develop comparably, efficient catalytic water purification techniques. This would not only make a contribution towards global environmental relief and protection of resources, but it would also strengthen the position of the German environmental industry in a market segment which has been neglected to date. However, it is important to note that whatever potential there is for

this approach, it will be limited by the fact that the magnitude of the parameter 'reaction temperature' which is available for gas phase catalysis is practically unavailable in the water phase.

To be carried out in a standard environment, all reactions must take place sufficiently quickly at temperatures between 15°C and 30°C.

A new field of activity for the chemical industry is the conversion of biomass into fuels and chemicals. In the process, large quantities of water are contaminated with organic compounds. Processing these water flows so that they can be recycled within the process or used for agricultural purposes is a new and challenging task for water treatment technologies.

Concrete challenges with a strategic importance are faced in the following areas:

- Increasing the selectivity and long-term stability of catalysts in order to reduce nitrates in groundwater and wastewater.
- Optimizing catalysts for the hydrodechlorination of chlorinated hydrocarbons.
- Development of catalysts for oxidation of ammonia or ammonium to nitrogen under mild reaction conditions.
- Expansion of the range of iron-based oxidation catalysts, e.g. by incorporation in zeolites.
- Development of colloidal reagents and catalysts which are suitable for *in situ* applications in contaminated groundwater aquifers – nanocatalysis.
- Development of catalysts for breaking down pharmaceuticals in hospital wastewaters.
- Combination of adsorptive enrichment of trace pollutants and their catalytic conversion.
- Protection of catalysts against being overgrown by biofilms and hence deactivated in long-term operation.

» In practice, catalysis in contaminated waters only has a chance if the catalyst systems offer sufficient long-term stability against a large number of possible catalyst poisons, particularly natural organic water components.

## 4.2. Treatment of industrial gases

The chemical industry in Germany has reduced the energy consumption per production unit by around a half since 1970, among other things through the use of modern catalytic processes. This means that catalysis makes a major contribution towards preventative environmental protection.

However, use of catalytic methods as a secondary measure is even more well-established than the role of catalysis for preventative environmental protection. With the aid of catalysts for air purification, a wide range of different emissions has been controlled for many years – particularly in the fields of transport and traffic (catalytic converters in car exhaust systems, see section 4.3.), emissions from power stations (flue gas desulfurization and denitrification), but also from a range of industrial and commercial applications. Today, the aim in most cases is to achieve or surpass legal limits on the emission of organic solvents, nitrogen oxides, SO<sub>2</sub>, dioxins or carbon monoxide. Here, the industry can fall back on decades' worth of experience with tried and tested catalyst systems.

In the future, the effects of global warming and associated climate change will push so-called greenhouse gases ever more sharply into public focus. Alongside carbon dioxide, this particularly includes methane and nitrous oxide (N<sub>2</sub>O), each of which has between 25 and 30 % of the climate relevance of CO<sub>2</sub>. Although both gases only occur in relatively low concentrations, their greenhouse effect per molecule is several times higher than that of carbon dioxide. Modern catalyst developments offer a significant potential here for a sustainable reduction of these greenhouse gas emissions as well.

One successful example which shows how catalysts are used to reduce greenhouse gases is the use of catalysts to reduce nitrous oxide from nitric acid plants, an application which today already accounts for savings of around 10 million tons of CO<sub>2</sub> equivalents per year.

Future strategic development lines in the field of exhaust gas after-treatment include:

- Widening of the catalytic reduction of greenhouse gases (e.g. methane, N<sub>2</sub>O) to new fields of application (combustion of sewage sludge, fluidized bed process, gas motors, cement and glass industry).
- Development of effective adsorption methods for volatile hydrocarbons from e.g. paintshops, printing

plants (enrichment with subsequent catalytic oxidation and possible recovery of solvents or thermal energy).

- Development of adsorption and oxidation processes for trace gases from the semiconductor industry.

- » Catalytic treatment of industrial waste gases is already highly established in industrial countries.
- » Improvements can be achieved in particular by combining multiple process steps.
- » There is potential for the development of new catalysts particularly in the areas of low-temperature reduction of NO and N<sub>2</sub>O and low-temperature oxidation of difficult-to-oxidize hydrocarbons, especially methane.

### 4.3. After-treatment of exhaust gases from internal combustion engines

Man-made changes to the Earth's atmosphere are the focus of an increasingly critical public debate. The debate centers on CO<sub>2</sub> emissions which give rise to the so-called greenhouse effect, along with emissions of carbon monoxide, hydrocarbons, nitrogen oxides and particulates, which are all potentially harmful.

A major proportion of the above pollutants comes from exhaust gases generated by internal combustion engines which are used to power motor vehicles. The desire of an increasing number of people for greater mobility means that these emissions are probably set to rise even further.

In order to reduce the effects of increased car ownership on man and nature, it is necessary to develop engines which consume less fuel, as well as improved exhaust gas purification systems (catalytic converters). These two different tasks should not be seen in isolation – instead, they need to be coordinated with each other, as improvements on the fuel consumption side have a direct impact on the composition of the exhaust gas. Due to the sensitivity of exhaust catalytic converters to sulfur, the fuel quality also needs to be brought into the equation.

In recent years, working in tandem with catalyst and fuel producers, the European automotive industry has managed to significantly reduce both fuel consumption and emissions. This has been made possible by the development of gasoline engines operating with a lean air/fuel ratio (i.e. under excess air conditions) with direct gasoline

injection, the optimization of diesel engines (which have always been operated with a lean air/fuel ratio and with direct fuel injection), the reduction of the sulfur content of fuels and the development of highly efficient exhaust gas purification systems.

For gasoline engines operating in lean mode, this meant that the traditional three-way catalytic converter had to be supplemented with a NO<sub>x</sub> storage unit in order to obtain sufficient reduction of NO<sub>x</sub>. Through the use of special barium materials for NO<sub>x</sub> storage, positioning the storage unit in a cooler location on the vehicle (underbody position) and the availability of low-sulfur gasoline (sulfur reduced to lower than 10 ppm), it has been possible to meet the thresholds imposed by the Euro 5 standards which came into effect in September 2009.

In the case of diesel cars, more powerful oxidation catalytic converters and improved soot filters have also been able to reduce the carbon monoxide/hydrocarbon emissions and the soot particulate emissions to below the strict Euro 5 limits. The additional fuel consumption required to burn the soot can be minimized through a catalyst coating on the filter.

In the case of trucks, an SCR (Selective Catalytic Reduction) catalytic converter containing vanadium has established itself as the best system for removing the nitrogen oxides which occur in higher concentrations when the engine is run in lean mode. The necessary infrastructure for the urea which is used as the reducing agent for this technology has been created. Thanks to the high efficiency of the SCR technology, fuel savings of up to 10 % are possible for trucks.

Further savings are absolutely essential in the future. For example, from 2015 onward the average CO<sub>2</sub> emissions from the car fleet of a manufacturer must not exceed 130 g/km per vehicle. For both gasoline and diesel engines, the key to further reductions is to further optimize the lean operating modes. The associated increase in NO<sub>x</sub> emissions and the necessarily lower exhaust gas temperatures will need to be overcome with more efficient catalysts. In order to comply with the Euro VI limits which will come into effect e.g. for trucks in 2013, it is now thought that a system will need to comprise at least the following four components: DOC, CSF, SCR and AMOX.

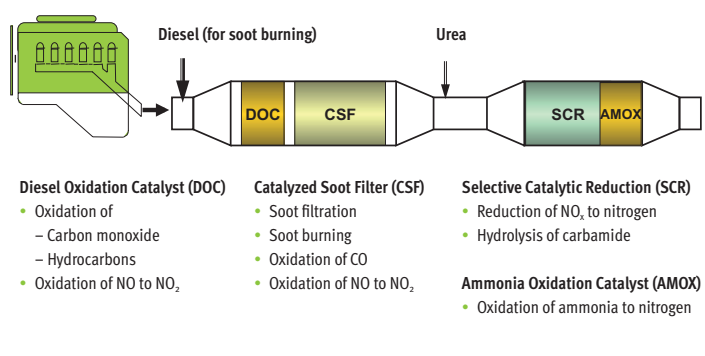


Figure 8: Purification of truck exhaust gases (Euro VI)

In order to realize such complex systems without excessively high costs for the end user, there is a huge demand for research in the following subject areas:

- Reduction of the precious metal content of the catalysts through improved understanding of sintering behavior.
- Lowering of the light-off temperature of oxidation catalysts.
- Development of long-term stable NO<sub>x</sub> storage catalytic converters which are already effective at low temperatures (in order to improve NO<sub>x</sub> storage) but can also be operated continuously at higher temperatures for improved removal of sulfur.
- Increased temperature stability of the catalyst carriers
- Catalyzed particulate filters which are so active during normal operation that soot is continuously burned off the filter.
- Increased use of modeling in order to reduce development times through better understanding of the physical and chemical interplay.

- » Compliance with future exhaust emission standards and a simultaneous reduction in fuel consumption is only possible with intensive cooperation between the manufacturers of catalytic converters, vehicle manufacturers and fuel producers.
- » The key to further fuel savings is the optimization of lean operation for both gasoline and diesel engines. Due to associated higher NO<sub>x</sub> emissions from the engine and the lower exhaust gas temperatures, it will be essential to develop more active exhaust gas catalytic converter systems.

## 4.4. Catalytic combustion

Catalytic combustion is a heterogeneously catalyzed gas phase reaction which has been one of the “classics” of heterogeneous catalysis since the invention of Döbereiner’s lighter. In contrast to the homogeneous gas phase reaction during the combustion process in flames, in a heterogeneously catalyzed combustion process the reacting substances (gases) and the catalyst (solid) are in different phases. The oxidation reactions take place on the surface of the catalysts, which mostly contain precious metals. Catalytic combustion processes not only deliver a rationalized and low-emission means of converting energy in burners, gas turbines, reformers and fuel cells, but can also be used for after-treatment of exhaust gases in stationary and mobile systems.



Figure 9: Döbereiner’s lighter  
(source: P. Amand Kraml, Kremsmünster Observatory)

Catalytic combustion offers important advantages over flame combustion in relation to reduced levels of pollutants and a higher degree of efficiency. Specifically, this relates to the following: the formation of nitrogen oxides is almost entirely eliminated for thermodynamic reasons due to the lower reaction temperatures; lower carbon monoxide and hydrocarbon emissions; high efficiency with a high rate of fuel conversion in excess of 99.9 %; good stability of the conversion process under fluctuations in the gas supply; large spread of air ratios; low operating temperatures.



Oxidation reactions are best catalyzed with metals from the platinum group of metals, but these are very expensive. The search for cheaper alternative catalyst materials has shown that relatively good catalytic activities can also be achieved with oxides and mixed oxides. In order to obtain large surface areas with a small quantity of material, the catalyst particles are finely distributed and applied to carriers. The carrier structures are made up of (among others) activated charcoal, diatomite or aluminum oxide with large internal surface areas and a high porosity. One of the biggest challenges here is to keep the high specific surface areas stable even under the high temperatures (gas turbine) which sometimes occur during the energy conversion process – even in long-term operation. Current development topics include approaches like barium hexaaluminate ( $\text{BaO} \cdot 6 \text{Al}_2\text{O}_3$ ) and other spinel structures, the structure of which is isomorphic to  $\gamma$ -aluminum oxide, mullite, mixed oxides based on ( $3 \text{SiO}_2 \cdot 2 \text{Al}_2\text{O}_3$ ) or mixed Al-Zr-Ce oxides which are further stabilized e.g. through Y or La doping.

During the last three decades, the development of catalytic combustion concepts has been driven forwards with particular intensity. In the process, work has focused on the development of new catalyst materials and carrier materials, as well as on the application-related layout of the burner design. Current challenges in the development of catalytic burners include improvements in terms of performance capability, improved long-term stability and the reduction of costs. Infrared emitters are important products for the application of heterogeneous catalysis in combustion processes, along with combustion chambers for stationary gas turbines and power plants. However, only few concepts have reached their goal and been launched to market. Mostly these are simple, robust systems which are designed as catalytic radiation burners and do entirely without a fuel gas/air pre-mixing stage. At present, a lot of different research activities are focusing on catalytic combustion under localized low-air conditions (rich-catalytic lean-burn combustion, RCL) in order to provide hydrogen and synthesis gas ( $\text{CO}$ ,  $\text{H}_2$ ) for gas turbines and for auxiliary power units (APUs) in vehicles. Here, variations in the chemical composition of the fuels, unsteady operating conditions (load changes, variation in the air/fuel ratio) and exhaust gas recirculation place special demands on the catalysts.

Significant applications for catalytic combustion which have already been launched to market include the purification of low-polluting industrial exhaust gases (see section 4.2) and the after-treatment of exhaust gases from internal combustion engines (see section 4.3). However, the

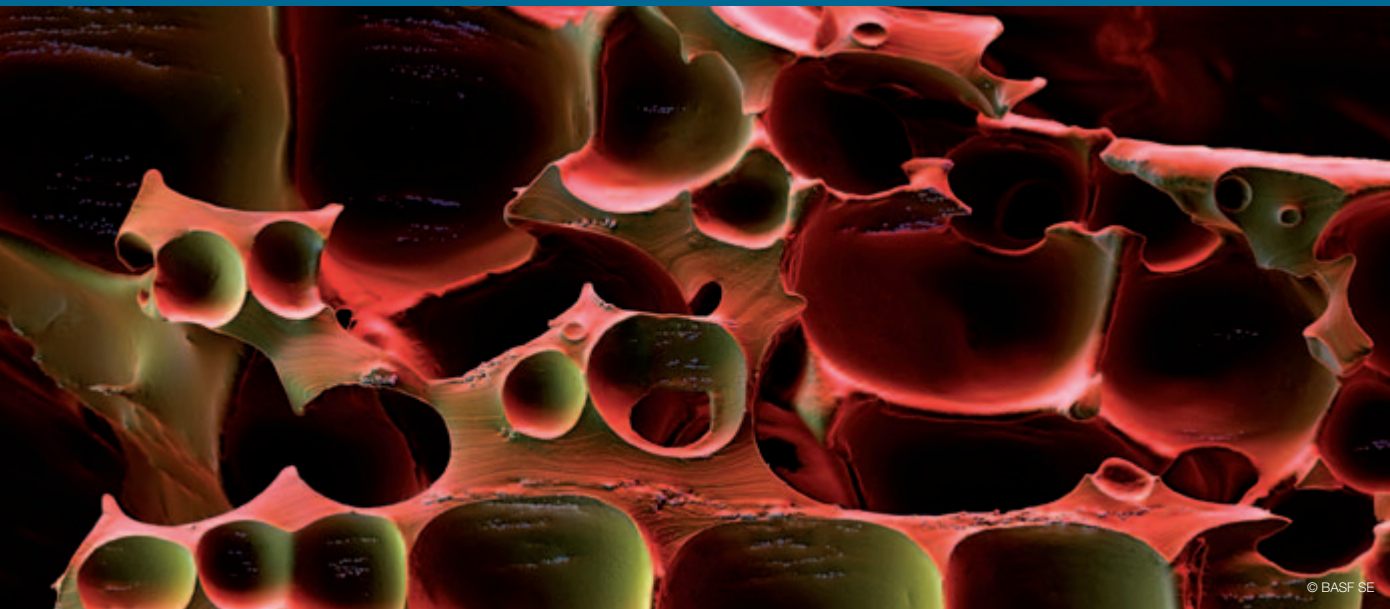
operating conditions in relation to fuel, concentration and temperature are very different here than they are in pure energy conversion systems. Particularly the use or admixture of natural gas and/or fuels produced from biomass results in exhaust gas compositions and temperatures for which no adequate catalyst systems are yet available.

Important fields of development with a strategic importance for catalytic combustion include:

- The development of precious metal-free catalysts and/or catalysts which require only a very low precious metal content on account of the use of suitable carriers and additives.
- Stabilization of the dispersion of active centers and/or suppression of agglomeration and sintering processes.
- The development of catalysts and/or carrier materials which offer high specific surface areas at application temperatures in excess of  $1100^\circ\text{C}$  for long periods of time.
- The development of robust catalysts for the combustion of methane at low temperatures, among other things for the after-treatment of exhaust gases on vehicles powered with natural gas.
- Catalysts for use in ignition boilers for petrol and diesel reformation, which are very robust and unsusceptible to catalyst poisons and coking.
- The development of compact burners and microburners for energy conversion, including in MEMSs (micro electromechanical systems).

- Catalytic combustion is an efficient form of energy production which only generates low levels of pollution.
- The conversion reactions for natural gas or biogas demand robust catalysts with excellent long-term stability.

## 5. Material- and energy-efficient processes



### 5.1. Production of monomers

Polymer materials are indispensable in almost all industrial sectors, with a wide range of applications as functional materials and body materials which is constantly expanding and constantly being redefined. They are used for example in the production of consumer products like dyes, paints, washing and cleaning agents, tires, textiles, glasses and contact lenses, automotive plastics, insulating materials or foamed materials. This means that, for many sectors of industry, commercial and technological progress depends to a large degree on technological advances in the field of polymer materials. This is defined in turn by the progress made in terms of catalytic processes and the availability of the necessary monomers.

As a general rule, polymers are made up of simple chemical monomers which are currently still primarily produced from fossil raw materials (crude oil) using catalytic processes. In the future, renewable raw materials will also become more important here. The key monomer building blocks are olefins (ethylene, propene, butene, butadiene, octene), which are polymerized into corresponding specialized, high-performance materials using catalytic methods. Copolymers play an important role here. Through polymerization of a basic building block molecule, e.g. an olefin, with one or more modifier molecules, it is pos-

sible to widen the range of potential applications of the polymer hugely. In addition, it is also possible to develop certain polymer/copolymer composites to selectively adjust the properties of the resulting innovative material to accurately meet the requirement profile of a particular application.

Today, the polymer industry faces the following fundamental challenges:

- For simple monomers, the challenge is to find more sustainable routes which can bypass the previous dependency on oil, as well as to improve the energy efficiency of established methods.
- For environmental and commercial reasons, process engineering faces the task of replacing catalytic liquid phase processes with solvent-free gas phase processes, which will require the development of innovative catalyst systems.
- The development of new techniques and catalysts for the production of monomer building blocks on the basis of new raw materials (e.g. methane → synthesis gas → methanol → olefins). Here, top priority goes to the improvement of zeolite-based MTO catalysts (methanol-to-olefins).

Alongside methanol as a C<sub>1</sub> source, it makes sense to develop more efficient synthesis routes to higher alcohols (propanol, butanol), so that these products can then be converted into olefins via catalytic dehydration. The primary objectives of catalyst development are: improvement of the mechanical stability of powdery and formed catalyst types, optimization of resistance to catalyst poisons and better control of product distribution and hence more efficient and therefore more sustainable utilization and recycling of raw materials.

- Processes and biocatalytic systems for the saccharification of lignocellulose into bioethanol as a raw material for ethylene.
- Single-step processes for the conversion of ethylene, preferably regenerative ethylene, into propene, e.g. via catalytic “one-pot” combination of ethylene dimerization/isomerization/metathesis into C<sub>3</sub> monomer.
- New methods and catalysts for heterogeneously catalyzed fixed bed synthesis of dimethyl carbonate for the polyurethane industry, starting from natural gas as an inexpensive and environmentally friendly raw material variant.
- New processes and catalysts for less energy-intensive capture of nitrogen in natural gas based hydrocarbons (acrylonitrile, caprolactam, amines, imines, aniline).
- Improved processes for dialkyl and diaryl carbonates starting from carbon dioxide.

- »» The shift in the availability of raw materials is forcing the development of new techniques for synthesizing classical and innovative monomers on the basis of natural gas, coal or renewable raw materials.
- »» More energy-efficient methods for monomer production and polymerization will be the central topics of catalytic and process engineering research and development.
- »» It will be important to develop efficient catalysts and processes for the production of higher alcohols, as they become increasingly important alongside methanol as basic C<sub>1</sub> building blocks as monomer precursors.

## 5.2. Tailor-made polymer materials and functional materials

Due to the enormous diversity of their material properties and their advantages, from a quantitative point of view polymers are the biggest organic end products in the chemical industry. With regard to carefully managed production and a longer-term shift in raw materials, polymers thus play a central role. The selective development of new polymer structures will require the application of catalytic processes.

Today, it is already possible to manufacture polyolefins with a desired microstructure with the aid of Ziegler catalysts, metallocene catalysts and other “single-site” catalysts. Alongside the molecular structure of the active centers, suitable carrier structures are significant for industrial polymerization techniques and for controlling the morphology of the product. Here, one of the challenges for the future is to develop improved catalysts which are also more temperature-stable, more resistant to aging and more cost-effective.

Another important challenge is the development of technically usable polymerization catalysts which enable the conversion of polar substrates and reactions in polar media. New routes to polymers which exploit the molecular structure of renewable raw materials will require a degree of tolerance to the functional groups containing oxygen which are present in fats, oils and carbohydrates. This will also open up access to materials and functional materials with innovative microstructures which to date have not been technically accessible. Suitable catalysts are also the key to the utilization of carbon dioxide as an ecologically and commercially advantageous building block for polymers.

Although catalytic methods allow many polymers to be made to measure and hence offer many different ways to improve material properties, processes for the copolymerization of nonpolar olefins with polar vinyl monomers like acrylates, vinyl esters, acrylonitrile or amides are in the domain of traditional radical processes. Even though encouraging progress has been made in this field recently, the development of catalysts which can be used on an industrial scale is a major long-term challenge. Aqueous emulsion polymerizations are applied on a large scale for the production of environmentally friendly water-based paints and coatings. Compared to these traditional radical methods, catalytic emulsion polymerization will enable the fine-tuning of microstructures and open up access to new emulsion polymerizates.

For industrial realization of e.g. paints which are more resistant to light and hydrolysis, improved, water-stable catalysts are once again the key. Catalysts which are insensitive to polar groups are also desirable for the direct production of macroscopic components with a controlled pore structure which can serve as carrier materials e.g. for chemical analysis.

To date it has not been possible to link copolymerizates from two or more building blocks with each other with a strictly defined sequence. Nature shows us the exceptional opportunities that this would open up, for example in the case of polypeptides which are made up of just 20 amino acids. As more than 100 monomers are available for these techniques, a corresponding ability to selectively combine these building blocks could result in polymers with unknown properties and potential applications we cannot even dream of yet. Undoubtedly, this type of copolymerization process will only be achievable in the long term with the aid of innovative catalysts.

New materials with an improved combination of mechanical properties, in particular modulus and impact strength, as well as innovative properties like conductivity, can be manufactured by incorporating nanofibers and nanoparticles in the polymer matrix. One possible technique would be to add functional groups to such nanoparticles and to polymerize them or provide for the uptake of soluble catalysts onto the surface of the particles and thus polymerize olefins and vinyl monomers. This would produce nanocomposites in which the nanoparticles would be dispersed in the matrix in non-aggregated form. Even under high levels of energy input, it is often not possible to achieve such a high degree of dispersity through retrospective incorporation of nanoparticles.

Important lines of development in the field of tailor-made polymer materials and functional materials include:

- » The selective development of new polymer structures will require the application of catalytic processes.
- » The development of innovative catalysts which are more temperature-stable, more resistant to aging and more cost-effective will enable the production of materials with a defined microstructure and morphology.
- » The use of renewable raw materials as the basis for innovative polymer materials and functional materials requires the development of catalysts with a degree of tolerance towards polar media.

- Catalysts for the production of innovative polymer materials and functional materials from renewable resources.
- Catalysts which are tolerant towards polar groups and reaction media for copolymerization and homopolymerization of polar monomers.
- The improvement of catalysts which enable the production of materials with a defined microstructure and morphology.
- Catalysts for sequentially accurate configuration of polymer chains.
- Catalytic integration of nanoparticles into the polymer matrix for the production of composites.
- The development of biodegradable polymer materials.

### 5.3. Conversion of synthesis gas to chemicals (GTC – gas-to-chemicals)

Synthesis gas is becoming an increasingly important platform both for the production of fuels like gasoline, diesel or kerosene, but also for the chemical industry in general, as in principle any raw material containing carbon can be synthesized via this interim stage. For coal as the source of carbon with the lowest hydrogen content, and therefore the most problematic raw material in terms of the climate – the long-term availability is assured. Crude oil will be replaced by natural gas as a raw material which is comparatively high in hydrogen. The conversion of biomass into synthesis gas is an alternative for the medium to long term.

The hydrogen requirements necessary to obtain the optimum CO/H<sub>2</sub> ratio depend on the raw material basis. As a general rule, it will be possible to adjust this ratio with the aid of watergas shift (WGS) technology. The most important development goals here are the development of highly selective catalysts with preferably minimized methanol selectivity, resistance to catalyst poisons and the reduction of the required reaction temperature, i.e. super low temperature shift catalysts, which will also find use in the reformer part of fuel cells among other things.

Regardless of the raw material basis, the decisive development goal for synthesis gas production is the optimization of reforming techniques. With maximized thermal

and mechanical loads being placed on the catalysts, there is a demand for improvements in terms of the mechanical stability and durability of the catalyst carriers, as well as for new concepts for optimization of and – in particular – for durable preservation of the dispersion of the active components, generally promoted nickel on oxides of aluminum, magnesium or combinations of these carrier materials.

Direct gasification of waste biomass into synthesis gas is technically and commercially not yet fully developed and still needs to be improved. Through partial pyrolysis it is possible to break down biomass into a petroleum-like hydrocarbon mixture which can be transported in liquid form and directly incorporated into the raw materials mix of refineries.

Established value chains based on synthesis gas follow a path via methanol to formaldehyde, acetic acid and MTBE. Consequently, methanol is one of the most important chemical raw materials. Worldwide production capacity totaled approximately 42 million tons in 2005, with worldwide consumption reaching 41 million tons in 2008. Methanol consumption of 50 million tons is forecast for 2012. Industrially relevant catalysts for methanol synthesis from CO and H<sub>2</sub> are often Cu/ZnO + metal oxide (metal = Al, Cr, Ti, Zr, as well as other promoters). One major challenge for the further development of catalysts for methanol synthesis is finding ways to prevent the system from being deactivated through sintering and sulfur poisoning.

The use of synthesis gas for oxo synthesis, the conversion of olefins with CO/H<sub>2</sub> into aldehydes and subsequent hydrogenation to the corresponding alcohols, is also well established. A constant challenge for oxo synthesis is to improve the recovery of homogeneous catalysts containing precious metals from the product mix as well as the control of the selectivity between linear and branched products.

New developments in synthesis gas based chemistry relate to an expansion of the methanol value chain on the one hand and the development of new direct synthesis methods on the other.

Methanol-based on-purpose olefin processes (MTO, MTP) for the production of short-chain olefins are currently at the industrial implementation stage. Ethylene and propene are important building blocks for the petrochemical industry with an annual production of approx. 110 x 10<sup>6</sup> t/a and 65 x 10<sup>6</sup> t/a respectively. In terms of the conversion of methanol to hydrocarbons, the deactivation of catalyst systems as a result of the formation of coke in the pores and the stability of the catalysts are the major technical stumbling blocks.

Depending on the process and catalyst type, up to a third of the activity is already lost in the first 1000 hours of operation. As well as uncovering the specifics of this deactivation mechanism, future research will also focus on its avoidance. Potential approaches for reducing thermal deactivation include among others the addition of

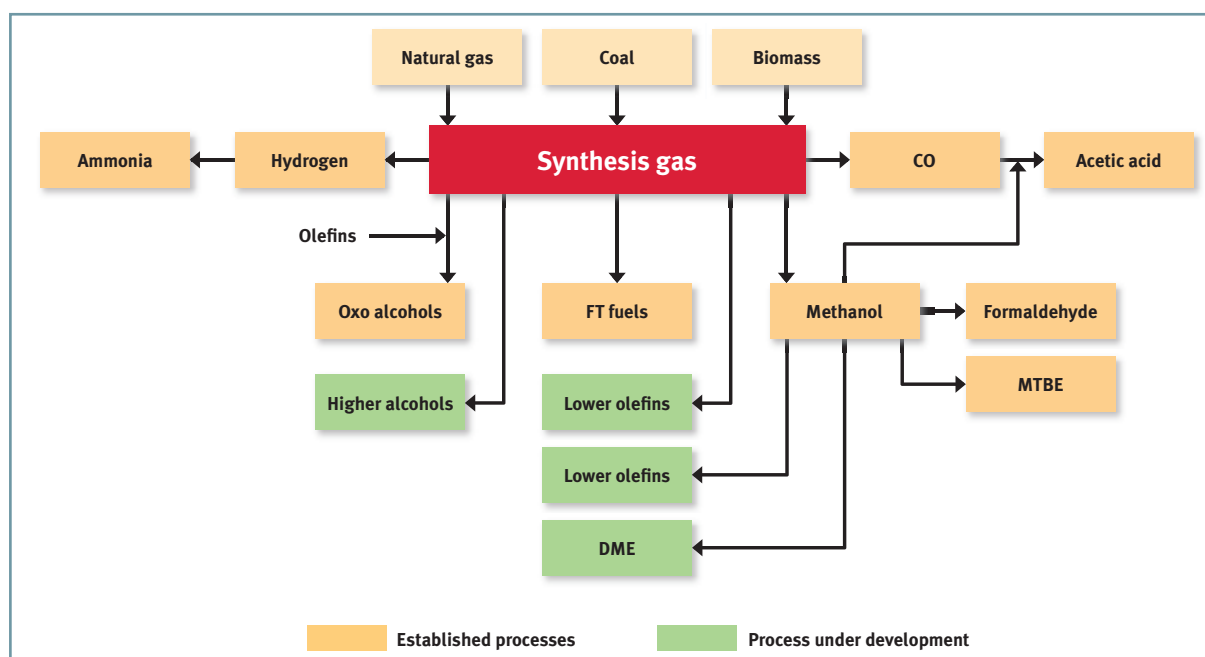


Figure 10: Synthesis gas flow chart

“spacer” materials (e.g. Al<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>) in order to achieve a mechanical spacing effect. In addition, challenges such as the improvement of CO activation also need to be overcome.

New markets for methanol are also opening up in the fuel market, either for direct use in alternative petrol fuels or as dimethyl ether as a synthetic diesel substitute.

Alongside methanol, the production of higher alcohols (HAS) from synthesis gas such as ethanol or isobutanol is of great interest. It is possible that significant progress will be made in the production of ethanol and isobutanol through selectivity and activity improvements.

As well as the important process of producing fuels using the classic Fischer-Tropsch method, direct olefin synthesis from synthesis gas is also becoming more and more important from an industrial point of view. What is attractive here is the fact that this route will open up access to alpha-olefins which at present are only generated as a by-product of fuel synthesis, where they have to be separated from the product mixture in a complex and time-consuming process.

There is a large demand for new catalyst systems in these last two fields in order to achieve a greater yield of the desired products.

- » Synthesis gas from a variety of different raw material sources (natural gas, coal, renewable resources) with an optimized CO/H<sub>2</sub> ratio achieved with the aid of improved watergas shift catalysts will represent one of the fundamental raw material sources of the future.
- » Priority areas of development are defined by the chemical stages which follow on from the synthesis gas production with new processes via methanol or directly to higher alcohols or olefins.
- » Continuous optimization of already established methods on the basis of synthesis gas (oxo synthesis, acetic acid, Fischer-Tropsch).

Following on from this, we have the following core research areas:

- Optimization of catalyst activity, selectivity and lifetime in the above-mentioned GTC processes, with more selective process control in the process in order to avoid broad product distributions.
- The development of highly selective, direct synthesis gas conversion processes into end products like hydrocarbons or oxygenates.
- Further development of methanol synthesis catalysts with performance criteria which are carefully selected to match the origin of the synthesis gas (coal, gas, biomass).
- Improved control of the watergas shift activity in order to avoid the production of CO<sub>2</sub> and the resulting methanation.

## 5.4. Fine chemicals

Fine chemicals are among the most important interim products in the chemical industry and in the life science industries. With the aid of corresponding modifications, a large number of fine chemicals and specialty chemicals is produced from the bulk chemicals, which are manufactured in quantities in excess of >100,000 t/a. Thanks to their functionality, fine chemicals are used as polymer additives and stabilizers, as dyes, vitamins, flavoring agents and in many other applications. In addition, they are important precursors for almost all known pesticides and pharmaceutical products. More than 10 million tons of fine chemicals are currently produced worldwide every year. Sections 3.1 and 3.2 take a closer look at the areas of dietary supplements/animal feed additives and enantiomerically pure precursors of active ingredients, where a number of important products are counted among fine chemicals.

While efficient catalytic processes in the fields of crude oil processing and so-called bulk chemicals are performed technically on a large scale (cracking processes, oxo reactions, oxidations, hydrogenations), to date direct and efficient catalytic processes for sustainable production of fine chemicals have not been properly realized in production processes. Factors which play a role here include the fact that these chemicals can often only be sold in the marketplace for a limited period of time and in comparatively small quantities.

As a result, the “time to market” is disproportionately more important in this segment than the development of a manufacturing process with a totally optimized yield. As a general rule, many fine chemical synthesis processes are still performed with classic organic reactions which have been established for more than 100 years, like nitration, Friedel-Crafts reactions and halogenation with co-production of stoichiometric – frequently hyperstoichiometric – quantities of salt waste. Furthermore, organic fine chemical synthesis is partially characterized by laborious protective group techniques (e.g. halogenation, dehalogenation) which are required for regioselective introduction of functionality. As a result, the established production processes often produce several tons of waste for each ton of target product. In the case of active ingredients, it is not unheard of for more than 100 times the quantity of product to be generated as waste. In this respect, there is great demand for the development of innovative catalytic methods which can be implemented swiftly and universally for new and environmentally friendly manufacturing processes. Where catalytic methods are already used, homogeneous catalysts and biocatalytic methods are chosen. The use of heterogeneous catalysts currently focuses on selective hydrogenation processes, reductive amination/alkylation processes and the acid-base catalysis.

The following core research areas deserve special mention:

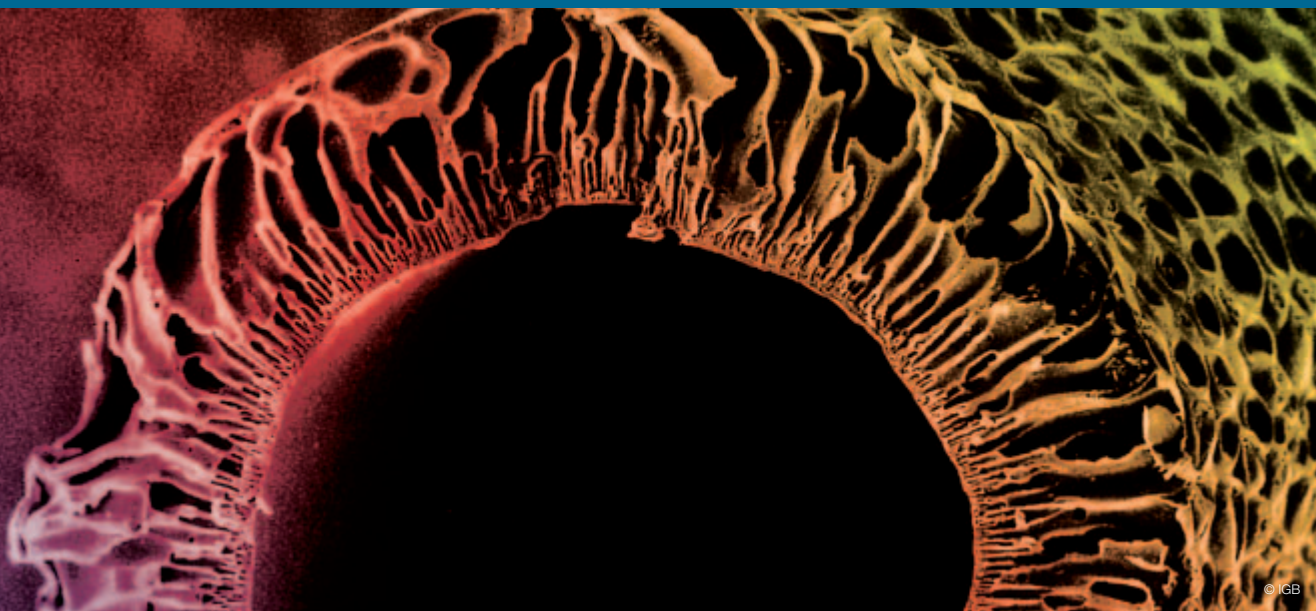
- Development of catalysts – homogeneous and heterogeneous transition metal catalysts, biocatalysts, organo-catalysts – in order to realize transformations which cannot succeed without a catalyst.
  - Development of synthesis methods in which biocatalytic stages are combined advantageously with conventionally performed catalytic stages.
  - Increased application of techniques such as high throughput screening (refer to section 7.2.) which enable faster production and market launch (“time-to-market”).
  - Introduction of new reactor technologies, such as microstructured reactors (refer to section 6.2.) which can offer higher efficiency and the possibility of reduced costs.
  - Reduction of the synthesis stages through the use of multifunctional catalysts.
  - Use of renewable raw materials.
- New approaches for direct regioselective and (in part) diastereoselective or enantioselective functionalization of aromatic compounds (hydroxy, amino, carbonyl and carboxyl groups).
  - Avoidance of (or at least reduction of) by-products in conventional reactions which are used in many applications (e.g. Friedel-Crafts reactions).

- To date, direct and efficient catalytic methods for sustainable production of fine chemicals have not been adequately implemented in production processes.
- There is great demand for the development of innovative catalytic methods which can be implemented swiftly and universally for new and environmentally friendly manufacturing processes for fine chemicals.

Reaction	Reagent in the stoichiometric method	By-product	Reagent in the catalytic method	By-products
Hydrogenation	E.g. $\text{LiAlH}_4$	$\text{LiAlO}_2$	$\text{H}_2$	None
Oxidation	E.g. $\text{CrO}_3$	$\text{Cr}^{3+}$ salts	Air	None
Alkylation	E.g. $\text{AlCl}_3$	$\text{Al}(\text{OH})_3$ , $\text{HCl}$	Zeolite surface	None

Figure 11: Comparison of stoichiometric and catalytic reactions

## 6. New reactor concepts



### 6.1. Multifunctional reactors/hybrid processes

The term 'multifunctional reactor' is used to describe e.g. the combination of a reaction stage with selective material separation in a device. Other concepts use the coupling of a catalytic reaction with selective excitation through plasma, light or microwaves.

#### Membrane reactors and catalytic membranes

The development of new membrane materials has highly energized this field in recent years. Examples with major technological and commercial potential include the following:

#### Production of synthesis gas with integrated air fractionation in a solid oxide membrane reactor

In a conventional synthesis gas plant, around 20-25 % of the capital outlay is spent on cryogenic air fractionation. Oxygen-selective, mixed conductive ceramic membranes would bypass the need for this part of the plant, thus making e.g. the conversion of natural gas into liquid fuels via synthesis gas significantly more cost-effective. The challenges here focus particularly on the development of the membrane and in the area of the reactor design. Catalysis plays an important role for two reasons: on the one hand, the speed with which oxygen is added

to and removed from the ceramic membrane is influenced by surface catalytic processes, and on the other hand the activity of the partial oxidation catalyst defines the partial pressure of the oxygen on the reaction side and hence the stability of the membrane material.

#### Integrated hydrogen separation (purification) in a membrane reformer

High-purity (i.e. CO-free) hydrogen needs to be produced especially for low temperature fuel cells. Conventionally, CO is removed from the reformat in several catalytic process steps. An H<sub>2</sub>-selective metal membrane would noticeably simplify this process and enable the construction of more compact devices. Although initial membrane prototypes have been built, these need to be significantly improved in terms of separating behavior, long-term stability and membrane costs. The integration of catalyst and membrane into a compact unit has also not yet been solved satisfactorily.

#### Performance of multi-phase reactions in a catalytic membrane contactor

Material transport inhibitions between reacting phases and within porous catalysts can limit the activity and selectivity of multi-phase reactions. Catalytic porous membranes are one approach to largely eliminating material transport inhibitions. Either the reaction mixture is



allowed to flow through the catalytic membrane, or the membrane serves to provide a defined contact zone between two fluid phases in situations with short transport paths from the phase limit to the active surface. Here, the porous structure of the membrane and the arrangement of the catalyst within the contact zone play a key role.

### Reactive distillation and adsorptive reactors

The simultaneous performance of reaction and material separation is particularly advantageous in equilibrium controlled reactions. The simultaneous separation of the reaction products from the reaction space allows almost complete conversion to take place. Compared to conventional methods, reactive rectification allows investment and operating costs to be lowered whilst the reaction turnover, selectivity and mass transfer are all improved. A whole range of reactive rectification processes is already being exploited in commercial applications, e.g. for the synthesis of MTBE or low esters. In these processes, it is important that on the one hand the phases required for material separation are present, and that at the same time the desired reaction takes place quickly enough under these conditions. The latter requirement often necessitates the use of suitable catalysts.

Instead of distillation, adsorption processes can also be exploited in order to separate materials; in conjunction with heterogeneous catalysis this leads to the adsorptive reactor. Here, it is possible to either adsorptively remove a product at the same time as the reaction is taking place,

or a starting material can be presented as an adsorbate. In the former case, the primary focus is on improving technical reaction parameters, such as turnover and selectivity, while – in addition to selectivity control – the use of starting materials in the supply stream despite their high degree of dilution provides the motivation in the latter case. The selection of a suitable adsorbent agent in terms of selectivity represents one of the most important design criteria for adsorptive reactors.

### Coupling of reactor and heat exchanger (wall reactor)

By coupling exothermic and endothermic reactions in a heat exchanger reactor, it is possible to realize autothermal reaction controls, as a result of which energy losses can be reduced. Here, e.g. the tubes of a tube bundle heat exchanger are coated with a catalyst and alternately charged with reactants. Rigorous further development of this reactor concept leads to microstructured reactors (see section 6.2.)

### Catalysis reactors with selective excitation

In principle, it is possible to positively influence the course of catalytic reactions through selective excitation in the form of plasmas, laser radiation, light or microwaves in suitably constructed reactors. Plasma-assisted catalytic exhaust air purification and photocatalytic purification of fluid phases have both reached a certain technical maturity – but in both cases non-selective total degradation reactions of the pollutants which are to be removed are accelerated.

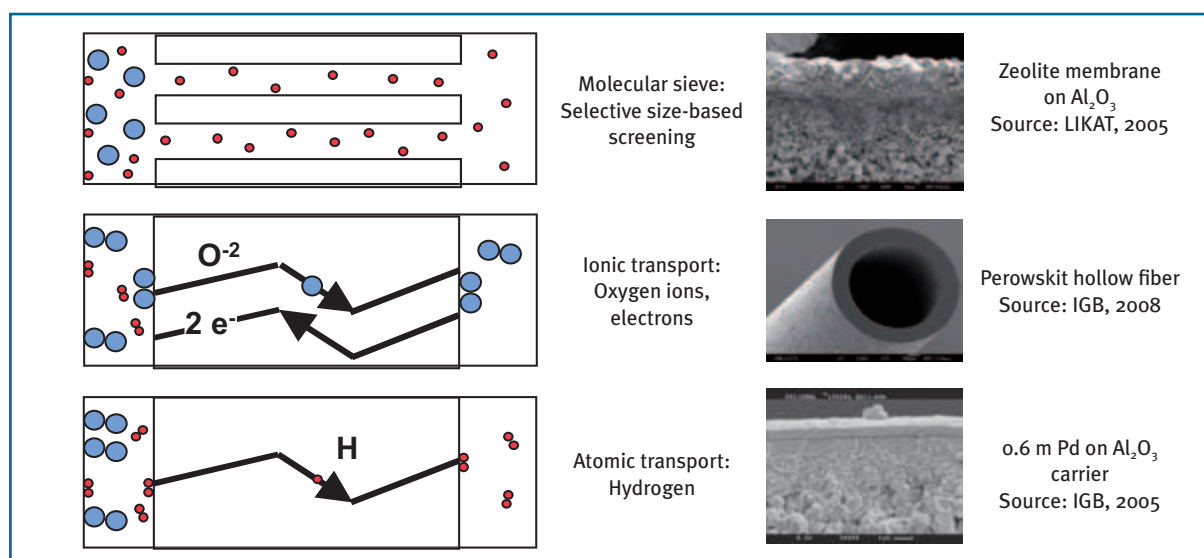


Figure 12: New inorganic membranes are temperature-resistant and resistant to chemicals, and their properties allow them to be used in catalytic membrane reactors at temperatures in excess of 400 °C.

The following development targets can be derived from the points discussed above:

- The development of selective membranes with high permeability which can be used e.g. in a membrane reformer even under high temperatures.
- New, cost-effective preparation techniques for multi-functional catalytic active membranes.
- The development of selective catalysts which enable the advantages of the membrane separation which is integrated in the reactor to be fully exploited.
- The development of catalytic systems with long-term stability which are permanently coupled to the membrane.

- » The coupling of material conversion and separation in a single device leads to more efficient processes.
- » Adapted catalysts are an essential factor for the effective operation of membrane reactors.

## 6.2. Microstructured reactors

The term ‘microstructured reactors’ should be preferred over the term ‘microreactors’, as it highlights the fact that only the dimensions of the flow channels in these reactors have to be small, but not the reactors themselves. The dimensions of the channels with different cross-sectional forms (round, rectangular, slit-shaped) are typically between approximately 100  $\mu\text{m}$  and a few millimeters.

The performance of chemical processes in these microstructures offers the following advantages:

- Heat and material transport are intensified towards the smallest dimensions, i.e. lateral temperature and concentration gradients are reduced. This makes it for example possible to prevent cold spots in heavily endothermic reactions and hotspots in heavily exothermal reactions.
- In conventional reactors, heavily exothermal reactions tend to run away, as a result of which they can often only be controlled by slow and controlled addition of the second reactant. In the latter scenario, the reaction is performed often far away from the optimum stoichiometry, which can have a negative impact on selectivity in mixture-sensitive reactions.
- With lower energy input, significantly larger specific phase boundaries (gaseous/liquid or liquid/solid) can be achieved than with conventional reactors, and this allows the mass transfer to be accelerated in catalyzed multi-phase reactions.

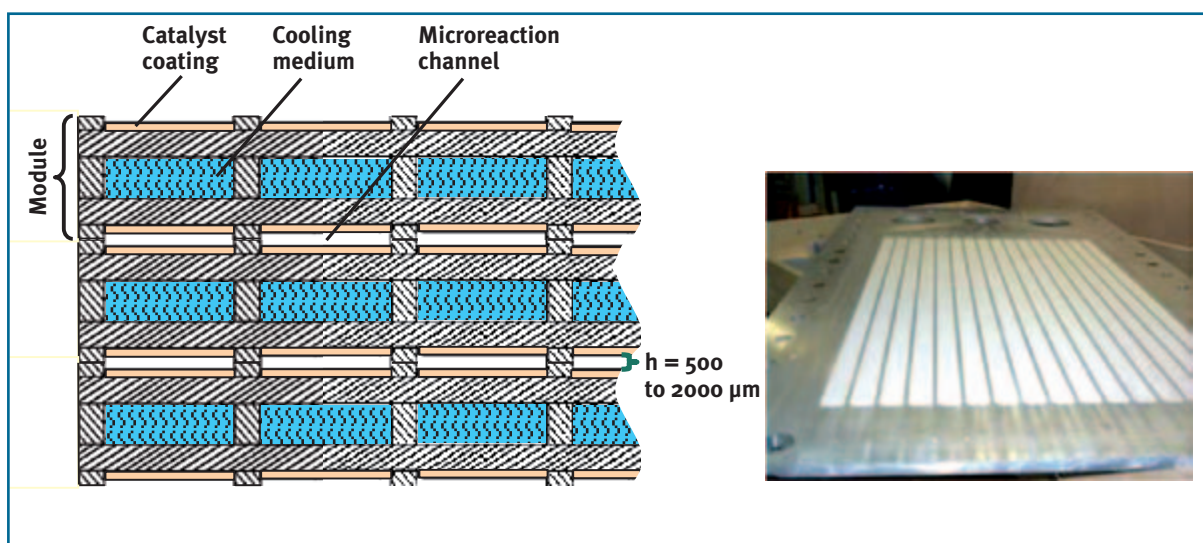


Figure 13: Microstructured reactor with catalyst coating according to the DEM IS® concept (left: schematic diagram, right: photograph of a coated module) (source: Uhde GmbH / Evonik Degussa)

- Chain explosions can be quenched by the high specific wall surface areas, i.e. the explosions can be suppressed.

The potential of microreactor technology can also be exploited in catalysis. To do this, the catalysts need to be adapted to the system. Great potential is associated particularly with heavily endothermic reactions, heavily exothermic and mixture-sensitive reactions and/or reactions which are problematic in terms of safety, as well as with multi-phase reactions. Investigations have progressed furthest in the case of heterogeneously catalyzed gas phase reactions. Here, the catalyst is used as a wall catalyst or in the form of a micro fixed bed.

It is a major challenge to achieve the high tonnages associated with bulk chemicals (> 100,000 tons per year). The necessary tonnages can be realized much more easily for catalyzed reactions in the liquid phase, which are often below 10,000 tons per year. The current estimate of the maximum known production capacity with microreaction technology is around a few thousand tons per year. The following specific development targets can be derived:

- For heterogeneously catalyzed gas phase processes, catalysts with significantly increased activity and same or higher selectivity compared to conventional catalysts are required in order to fully exploit the potential of microreaction technology.
- For catalyzed liquid phase reactions (heterogeneous catalysis, molecular catalysis and biocatalysis), experimental and theoretical investigations are needed in order to be able to technically assess the potential of these systems.
- Methods and correlations for the design of catalyzed processes in microstructured reactors both in terms of reaction technology and technical safety.

- » In microstructured reactors it is possible to run catalyzed reactions at the kinetic limit, i.e. the reactor (material and heat transport) does not limit the catalyst output.
- » New high-performance catalysts, new process windows and new synthesis routes are needed in order to fully exploit the potential of microstructured reactors..

### 6.3. New reaction media

The choice of solvent plays a vital role for the chemical reaction and its technical implementation in a catalytic process. Organic solvents are often used here, but there are significant objections to the use of these solvents for reasons relating to the environment, toxicological concerns and technical safety issues. The complete separation of the solvents from the products and their recycling (via a material cycle) or disposal also represent major factors in terms of process costs. The solvent can intervene in the catalysis cycle at a molecular level and thus influence activity and selectivity. In general, very little is known about this from a mechanistic point of view. As a result, in the development of sustainable catalytic processes special importance is placed on the search for new solvent concepts.

The systems described below are of particular interest from a scientific and process engineering point of view as innovative solvent concepts for catalysis. In addition, there are also other interesting strategies for avoidance of the use of organic solvents, e.g. by using thermoregulated systems in which separation processes can be induced through changes in temperature.

Ionic liquids are low-melting salts of organic cations and suitable anions which are liquid in the temperature range of typical organic reactions. They have an extremely low vapor pressure, which can be exploited in innovative separation methods. As they are entirely made up of charged particles, strong interactions can result at molecular level which often produce unique characteristic profiles. The property of certain ionic liquids to dissolve biopolymers (such as cellulose) and even complex biopolymer mixtures (such as wood) completely and with a relatively high capacity (up to 20 mass percent) is of particular interest here. This opens up new possibilities for the catalytic conversion of biogenous raw materials. Another interesting development in recent years is the so-called 'supported ionic liquid phase' (SILP) catalysis. Here, a thin film of a catalytic active ionic fluid is coated onto a highly porous carrier. The resulting solid can be processed in the same way as a classic heterogeneous catalyst, while the active center is present in a homogeneously dissolved form in the non-vaporizable fluid.

Supercritical fluids have physical and chemical properties which can be described as a combination of the properties of the gaseous phase and the liquid phase. Supercritical carbon dioxide and supercritical water are particularly interesting from an ecological and commercial point of view.

Supercritical carbon dioxide is already used in large-scale technical applications in the extraction of natural substances (decaffeination of coffee and tea).

Water is a preferred solvent from an ecological and commercial point of view, but the solubility of many organic substances and most gases in water is only limited. This “disadvantage” can be exploited in the so-called two-phase catalysis for catalyst separation.

In some cases, the chemical and physical properties of these systems differ significantly to those of established organic solvents. Consequently there is a great demand for research into the development of catalytic processes in relation to these media. The following specific development targets can be derived:

- The synthesis of specific catalysts which are adapted to the properties of the new reaction media.
- New process engineering concepts for recycling catalysts.
- Understanding of the interaction between catalyst and solvent system at molecular level.

- » New solvent concepts will play a particularly important role in the development of sustainable catalytic processes.
- » The chemical and physical properties of alternative solvent systems differ significantly to those of established organic solvents.
- » A lot of research still needs to be done in order to fully unlock the application potential of new reaction media.

## 7. New investigation and preparation techniques

For the optimization not only of catalysts, but also of overall processes, an understanding of how the catalyst behaves under reaction conditions is a valuable tool. In conjunction with new preparation techniques and scale-independent modeling, online measuring techniques provide an insight into the action mechanisms and a fundamental understanding of catalytic reactions, which in turn provides key pointers for optimization approaches.



### 7.1. Nanostructured catalysts

Nanostructured materials often have different properties compared to the bulk material with the same composition; in extreme cases of very small nanoparticles, the electronic structure can display size quantization effects. While the development of nanostructured materials usually focuses on one specific material property, and not every nanostructured material is intrinsically effective as a catalyst, nanoparticles contained in catalysts contain a significant number of atoms with coordinatively unsaturated sites (so-called CUS centers or defect structures) in comparison to the bulk structure. Particularly this type of center, which includes atoms in corner, edge and terrace positions as well as dislocations, is important for catalytic functions and characteristic of many catalysts used in chemical engineering; here, the particle size of the active components (e.g. metals, oxides) is often in the range of 1-10 nm. The activity of catalysts is particularly high if the central property of nanostructured particles, i.e. the stabilization of non-equilibrium forms of the material (e.g. defect structures, multiple twin particles, lattice stresses of a phase), comes into play – and specifically if this happens under the reaction conditions and ambient conditions (reactive gases, solvents) of the chemical reaction

or chemisorption under consideration. This also explains the frequently observed dynamic behavior of nanostructured catalysts (deactivation, sintering of fine-particle sized particles), which is accompanied by reversible and irreversible changes in nanoparticle size, shape and morphology as well as the interaction with the carrier material. As a result, there is therefore a considerable range of different building blocks of nanostructured catalysts, and one of the tasks of modern catalysis research is to explore their synthesis (structuring over multiple orders of magnitude in scale using chemical methods) and verification (chemical analysis of structure-forming processes under *in situ* conditions) in this field.

We currently have a command of nanostructuring in the synthesis of carrier materials, e.g. of mesoporous systems, zeolites and coordination polymers (MOFs). So that this can be widened to the nanostructuring of catalysts (e.g. metal/carrier, mixed oxides), we need a much better understanding of the options afforded by target-oriented product controlling during catalyst synthesis. In the process, it is to be expected that the checking of the building blocks which control the (nano)structure in the carrier matrix will also contribute to the development of defined single-site catalysts.

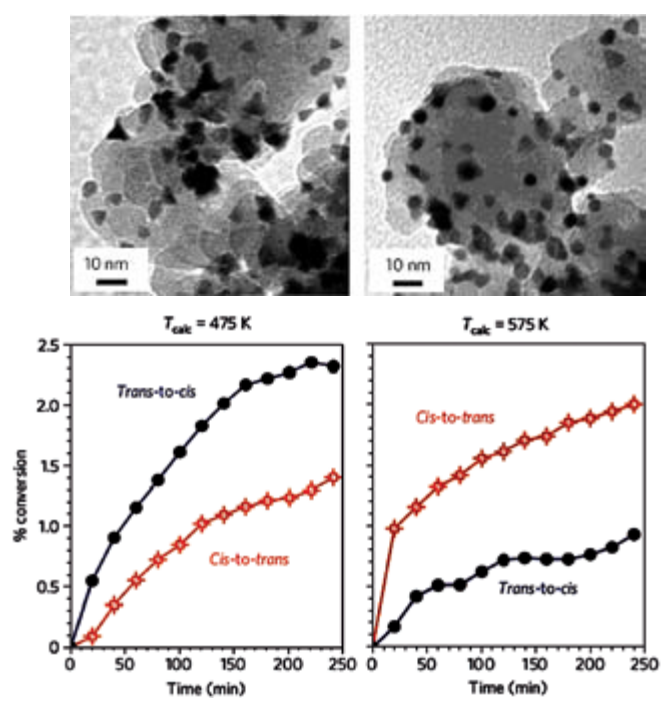


Figure 14: Temperature change during calcination: influence on the particle form but not on the particle size of the platinum nanoparticles carried on SiO<sub>2</sub>. This leads to a reversal of the selectivity of the reaction. (I. Lee, F. Delbecq, R. Morales, M.A. Albitar, F. Zaera, Nature Materials 2009)

Other promising approaches for chemocatalysis are aimed at the development of nanostructured catalysts from defined molecular, in particular organometallic, catalyst precursor compounds, the use of preformed metal (hydr)oxide colloid/carrier systems (e.g. PVP-stabilized, supported PdOxHy particles), nanostructured carbon-based materials and conductive polymers (e.g. polyaniline).

- » Selective design of the catalyst surface/morphology with a large number of atoms with coordinatively unsaturated sites delivers highly active catalysts and can open up new reaction paths.
- » The development of nanostructured catalysts requires chemical structuring processes across several orders of magnitude in scale and verification of the structure-forming processes, and therefore a molecular understanding of the real structure.

## 7.2. High-Throughput-Experimentation

During the last decade, the field of high-throughput experimentation (HTE) has become firmly established in a wide range of different branches of industry. The term is

used to bring together different methodologies which significantly accelerate research and development of catalyst synthesis and testing and in this way help to speed up the overall development of new and more efficient industrial processes. The methodology originates from pharmaceutical research carried out to discover new active ingredients, but for applications in the field of catalysis it was mostly necessary to develop new solutions. There are plenty of success stories in which catalysts and processes discovered with the aid of high-throughput technology are already in the pilot phase or, in some cases, are already being used in production (e.g. Symyx/Dow polyolefin catalyst or hte/CRI catalyst for the production of styrol). The key components which contribute to the success of the HTE concept are high-throughput synthesis and testing, efficient data management and automation. Of these, high-throughput synthesis undoubtedly presents the greatest challenge, as there are a large number of catalytic materials with different properties which build upon diverse and in some cases highly complex preparation and after-treatment steps. The skill here is to obtain the same catalyst as an experienced synthesis scientist while using efficient automation techniques and, in addition, to define the relevant parameter range very systematically. One important development goal here is to design further robust synthesis tools which will significantly reduce the complexity of and effort involved in the synthesis process. By contrast, high-throughput testing, data management and laboratory automation have already reached a relatively high standard of technical development. However, particularly in the case of online chemical analysis, there is still a need for faster, stable methods in order to reliably obtain a high level of detailed information. Close cooperation between industry and scientific institutions is essential in order to jointly contribute to our understanding of catalysis and thus master the constant challenges from the development of materials right up to scale-up and application. On the basis of a systematic database, generic approaches need to be developed both for synthesis and testing, so that structure-effect relationships which offer long-term reliability can be established with the aid of modeling techniques, e.g. with ab initio techniques.

Two trends can currently be observed in HTE research. Firstly, there is an increasing demand for multi-purpose reactor systems with a high degree of flexibility, which cover a wide range of chemical reactions and hence also a wide range of reaction conditions. Secondly, there is also a shift towards the sub-pilot scale. These larger reactor systems are used to obtain data of sufficiently high quality for kinetic modeling and to be directly correlated with data from the pilot plant.

In the field of laboratory automation, new components, integrated modules and other new developments are constantly being launched onto the market. Development work needs to be carried out on applications which demand the individual linking of several isolated solutions to a combined solution. In many branches of industry, this type of “integrated workflow solution” is desirable beyond the field of catalysis, such as e.g. in the consumer goods industry or coatings research, although they require a relatively high level of investment for the companies involved. Consequently, the corresponding technical fields require more cost-effective, modular solutions which are flexible in terms of applications and can easily be expanded or upgraded in the future.

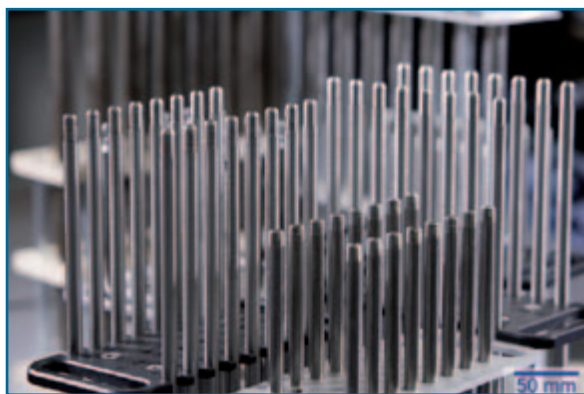


Figure 15: Various flow reactor tubes prior to installation in the high-throughput experimentation system (source: hte AG)

Progress can also be observed in the development of suitable data management systems. Continuing work also needs to be done in terms of the appropriate representation of catalysts in databases, the development of adapted data analysis systems and in relation to methods for intelligent, software-assisted library design. This technology component will have a major role to play in the broader success of the concept in the future. Further topics for continuous improvement of the currently available software solutions include: interconnectivity of multiple, parallel databases, user-friendliness of the software, harmonized interfaces to other software products and standardization of data structures.

Further development of high-throughput technology faces the following challenges:

- Development of intelligent data management systems
- Development of synthesis strategies for automated catalyst synthesis
- Further improvements to online analysis tools
- Use of high-throughput technologies in later stages of process development
- Development of operando methods of catalyst characterization for high-throughput experimentation.
- Development of techniques for fast determination of optimum reaction conditions and procurement of kinetic data (vs. high-throughput techniques for catalyst “discovery” (hits) in the past).
- Development of automated laboratory solutions with a modular and flexible structure.

- » The close integration of synthesis, testing and data evaluation in a workflow forms the key to success.
- » There are trends towards larger high-throughput experimentation systems which can be flexibly used to obtain kinetic data which can be directly correlated with data from the pilot plant.

### 7.3. *In situ* methods

Knowledge-based and hence time-effective catalyst design, which goes beyond the scope of the empirical methodology being currently still dominating, requires a scientific understanding of the relationship between the structure and mode of action of catalysts on the one hand and the influence of synthesis parameters on these properties during catalyst synthesis on the other. Both pieces of information must be obtained under at least approximately real reaction conditions.

There is now a variety of measuring techniques available for *in situ* investigations of catalysts.

Examples include infrared (IR) and Raman spectroscopy, spectroscopy in the ultraviolet and visible range (UV-vis), electron spin resonance (ESR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, X-ray absorption spectroscopy (XAS), diffraction of synchrotron or neutron radiation, along with a number of other techniques.

The term “operando spectroscopy” has been introduced for methods which allow structural data and catalytic

information to be obtained simultaneously. In this case, the analytical cell operates as a catalytic reactor which is coupled to an online product analysis. In comparison to the monitoring of catalytic reactions, *in situ* studies of catalyst synthesis processes are underrepresented to date. However, this type of investigation bears interesting potential for fine-tuning catalyst properties through optimized synthesis protocols.

The ways in which catalysts work are highly complex, but the various analytical methods only deliver a specific part of information. As a result, in order to gain a comprehensive understanding, several methods will need to be employed – ideally in the same experiment and under identical conditions. This does not only save time, but increases markedly the overall level of knowledge which can be gained. Moreover, it avoids artifacts which can result from

differences in cell geometry. Examples of the simultaneous coupling of several *in situ* methods include EPR/UV-vis/Raman spectroscopy, XAS/Raman/UV-vis spectroscopy, as well as couplings of FTIR spectroscopy with thermal analysis, Raman or UV-VIS spectroscopy for heterogeneous catalytic gas phase reactions. Recently, the coupling of five spectroscopic techniques was achieved using the synchrotron radiation source BESSY, and this was used to study the synthesis of molybdate catalysts.

Due to the need for extensive equipment, particularly in terms of instrumentation, permanent centers should be established for the techniques for *in situ* characterization of catalysts, for example in the form of fixed experiments on synchrotron radiation or neutron sources, or also dedicated NMR systems.

For the *in situ* characterization techniques, future lines of development will focus particularly on the following fields:

- Further development of analytical operando techniques for solid catalysts under process-relevant conditions (pressure, temperature, flow reactors, coupling with online product analysis), with coupling of several operando methods for simultaneous investigation of a sample under identical conditions.
- Adaptation and development of methods for the investigation of solid/liquid phase reactions and/or solid/gas/liquid phase reactions. To date, most *in situ* and operando investigations have been restricted to gas phase reactions over solid catalysts under normal pressure conditions or in vacuum.
- Adaptation of *in situ* methods for online monitoring of catalyst syntheses.
- Parallel investigations in high-throughput setups.
- Enhancement of time and spatial resolution of spectroscopic operando methods (coupling of operando spectroscopy and microscopy), including the development of fast evaluation and simulation software.
- Development and optimization of new operando methods for monitoring homogeneous catalytic processes, including suitable methods for model-free deconvolution of spectra.

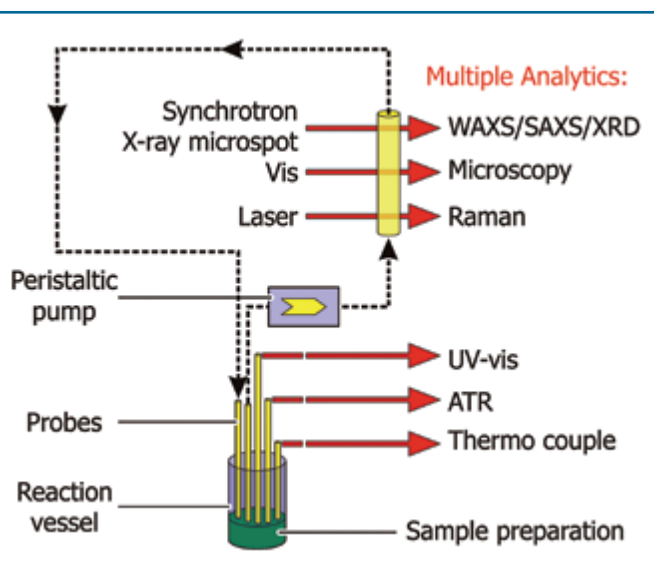


Figure 16: Schematic diagram of the experimental arrangement for simultaneous WAXS/SAXS/Raman/ATR-FT IR/UV-vis measurements during catalyst synthesis at the  $\mu$ -spot beamline of the BAM at the Berlin synchrotron ring BESSY.

- Selective, knowledge-based design of catalysts is only possible with in-depth knowledge of their mode of action.
- The realization of realistic reaction conditions in the exploration of structure-reactivity relationships is essential for the results to be relevant, and this is only possible with the use of *in situ* and operando methods.
- Advancements in terms of increased time and spatial resolution of the methods and the ways in which they are coupled, including theoretical approaches, will play a pivotal role in the knowledge gain for the design of new, highly capable catalysts.



#### 7.4. Scale-independent modeling: from quantum chemical calculations to reactor modeling

Theoretical methods have been established for many years on various levels in catalysis. Even back in the infancy of catalysis, microkinetic models were drawn up, after which the increasing processing power of computers allowed the development of fluid dynamic simulations and quantum chemical calculations. However, we are still some way off comprehensive modeling of a reactor in which catalytic reactions take place.

At the level of the catalytic reaction itself, significant progress in terms of our fundamental understanding of catalytic steps has been made with the aid of the methods of density functional theory which have been available for around 20 years. These types of calculation form the basis (the atomic scale) for multi-scale modeling. Accurate quantum chemistry *ab initio* methods (or also the quantum Monte Carlo method) are important for validations, but the calculations are so complex that they can rarely be used on real systems. In fact, the quality of density functional theory calculations has reached the point where it is now possible not only to interpret experimental findings retrospectively, but also to often make genuine predictions. However, development work still needs to be done in terms of describing the van der Waals interaction, excited electronic states and non-adiabatic processes. The theoretical treatment of the chemistry of rare earth compounds, which could play an even more important

role than catalysts in the future, also remains unsatisfactory. Due to the limited number of atoms involved in the active center, the ability of the models to deliver meaningful predictions is higher for homogeneous catalysis than it is for heterogeneous or enzyme catalysis. An increasingly important role will be played by hybrid methods, in which only the active center is described with accurate *ab initio* methods, while density functional methods or electrostatic fields are used to describe the surroundings.

The development of microkinetic models based on detailed knowledge of the reaction mechanisms has already profited from quantum chemical calculations, even though efforts in this field still have to rely on extensive experimental investigations in many cases. The kinetics used for the design of reactors generally still contain empirical equations; this is also linked to the fact that material and heat transport effects are usually superimposed onto the reaction. Whereas we often used to use analytical approximation methods, today complete models are solved exclusively through numerical integration of the corresponding systems of equations.

Finally, at the level of the reactor, fluid dynamic simulation methods which can now be performed on desktop computers have revolutionized the design of reactors in the last 10 years. For example, it is now possible to locally model the flow conditions in reactors in 3-D. Finite element methods were conventionally used for this purpose, but an alternative is now available in the form of lattice Boltzmann methods; this approach appears to be very

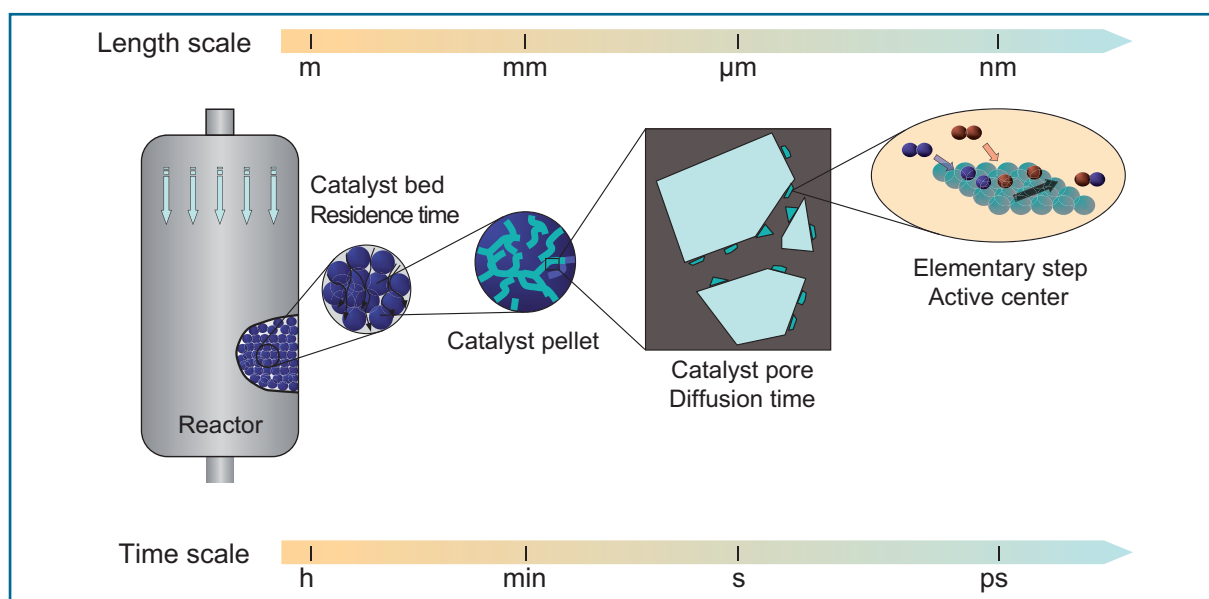


Figure 17: Catalysis is a multi-scale phenomenon with a complex interaction between the reaction and material transport across all length and time scales.

promising for the modeling of complex geometries, as in this case the complexity of the calculations does not increase with the complexity of the flow conditions.

It is difficult to anticipate developments in the next few years, as although various problems have been identified (e.g. non-adiabatic processes, inclusion of heat transport on a microscopic scale), no breakthroughs are in sight yet in terms of theoretical treatment. Another important step must be to port the existing computer programs, which are hugely complex, onto massively parallel computers. This will involve more than 100,000 processors in the next 10 years, so it will require major reprogramming and the development of new types of algorithm. If this turns out to be successful then new fields of application will also be unlocked. One important line of development is the coupling of quantum chemical methods with approaches from the field of molecular mechanics (QM/MM coupling), which now already allows us to calculate complex systems like the active center of enzymes in an aqueous environment with a good degree of accuracy. This could also open up access to high-quality theoretical calculations of processes like solid-catalyzed reactions in the liquid phase.

Multi-scale modeling requires clean linking of various different methods, whereby no uncontrolled errors must be allowed to creep into the models. Starting from the density functional theory (with the possible addition of quantum chemical or quantum Monte Carlo methods for improved treatment of the correlation), the quantum chemical information flows into an ab initio molecular dynamic. The resulting information can then be used for a kinetic Monte Carlo simulation (kMC). For simple systems this describes scales up into the range of micrometers and minutes. While it is, in principle, possible to make available the physical parameters (activation barriers for reactions and diffusion on/at the surfaces, steps, edges and corners) required for kMC simulations through a multitude of DFT simulations, it is possible with the aid of kMC simulations of a large number of catalyst particles to derive ki-

netic approaches for describing the macroscopic reaction speeds as a function of the local chemical composition of the fluid and solid phases and the temperature. However, problems relating e.g. to microscopic heat transport and non-adiabatic processes remain unsolved here. The description, which has been atomistic up to this point, now needs to be linked to fluid dynamic simulations (computational fluid dynamics, CFD). Unsolved problems remain here in terms of reversible linking of the different methods and the determination of possible errors. In the event that these linking attempts prove successful, we would have achieved scale-independent modeling from the events at molecular level to the technical reactor level.

The following lines of development have been identified:

- Theoretical understanding of catalytic processes through quantum chemical treatment and simulation of sufficiently large model systems with the necessary precision.
- Theoretical description of complex catalytic systems through QM/MM coupling.
- Integration of quantum chemical methods and thermodynamics/statistical mechanics in order to understand the catalyst under reaction conditions.
- Integration of quantum chemical methods, microkinetics and reactor modeling for a comprehensive theoretical description of catalytic processes.

- » Theoretical calculations make a valuable contribution towards our fundamental understanding of catalytic reactions and therefore towards the development of new catalysts and methods.
- » Scale-independent modeling of catalytic processes from the events at molecular level to technical reactor level requires the integration of quantum chemical methodology, microkinetics and reactor modeling.

## 8. List of authors

The German Catalysis Society GeCatS wishes to thank the following people for their help in preparing this document:

<b>Prof. Dr. Matthias Beller</b>	Leibniz Institute for Catalysis, Rostock
<b>Prof. Dr. Angelika Brückner</b>	Leibniz Institute for Catalysis, Rostock
<b>Dr. Karsten Büker</b>	Uhde GmbH, Dortmund
<b>Prof. Dr. Jürgen Caro</b>	Leibniz University Hanover
<b>Prof. Dr. Peter Claus</b>	TU Darmstadt
<b>Dr. Dana Demtröder</b>	DECHEMA e.V., Frankfurt
<b>Dr. Dirk Demuth</b>	hte Aktiengesellschaft, Heidelberg
<b>Prof. Dr. Olaf Deutschmann</b>	University of Karlsruhe
<b>Prof. Dr. Rainer Diercks</b>	BASF SE, Ludwigshafen
<b>Dr. Richard Walter Fischer</b>	Süd-Chemie AG, Bruckmühl
<b>Prof. Dr. Frank Glorius</b>	University of Münster
<b>Dr. Christoph Gürtler</b>	Bayer MaterialScience AG, Leverkusen
<b>Dr. Daniel Herein</b>	Umicore AG & Co. KG, Hanau
<b>Prof. Dr.-Ing. Elias Klemm</b>	University of Stuttgart
<b>Prof. Dr. Frank-Dieter Kopinke</b>	Helmholtz Center for Environmental Research – UFZ, Leipzig
<b>Prof. Dr. Udo Kragl</b>	University of Rostock
<b>Prof. Dr. Walter Leitner</b>	RWTH Aachen University
<b>Prof. Dr. Johannes August Lercher</b>	TU München
<b>Prof. Dr. Andreas Liese</b>	Technical University of Hamburg-Harburg
<b>Dr. Marco Lopez</b>	Umicore AG & Co. KG, Hanau
<b>Prof. Dr. Stefan Mecking</b>	University of Konstanz
<b>Dr. Josefin Meusinger</b>	Adam Opel GmbH, Rüsselsheim
<b>Prof. Dr. Martin Muhler</b>	Ruhr University Bochum
<b>Dr. Friedbert Nees</b>	BASF SE, Ludwigshafen
<b>Prof. Dr. Joachim Sauer</b>	Humboldt University Berlin
<b>Prof. Dr. Matthias Scheffler</b>	Fritz Haber Institute of the Max Planck Society, Berlin
<b>Prof. Dr. Ferdi Schüth</b>	Max Planck Institute of Coal Research, Mülheim
<b>Dr. Ekkehard Schwab</b>	BASF SE, Ludwigshafen
<b>Dr. Kurt Wagemann</b>	DECHEMA e.V., Frankfurt
<b>Prof. Dr. Peter Wasserscheid</b>	University of Erlangen-Nuremberg
<b>PD Dr. Dorit Wolf</b>	Evonik Degussa GmbH, Hanau
<b>Dr. Ralf Zuber</b>	Umicore AG & Co. KG, Hanau

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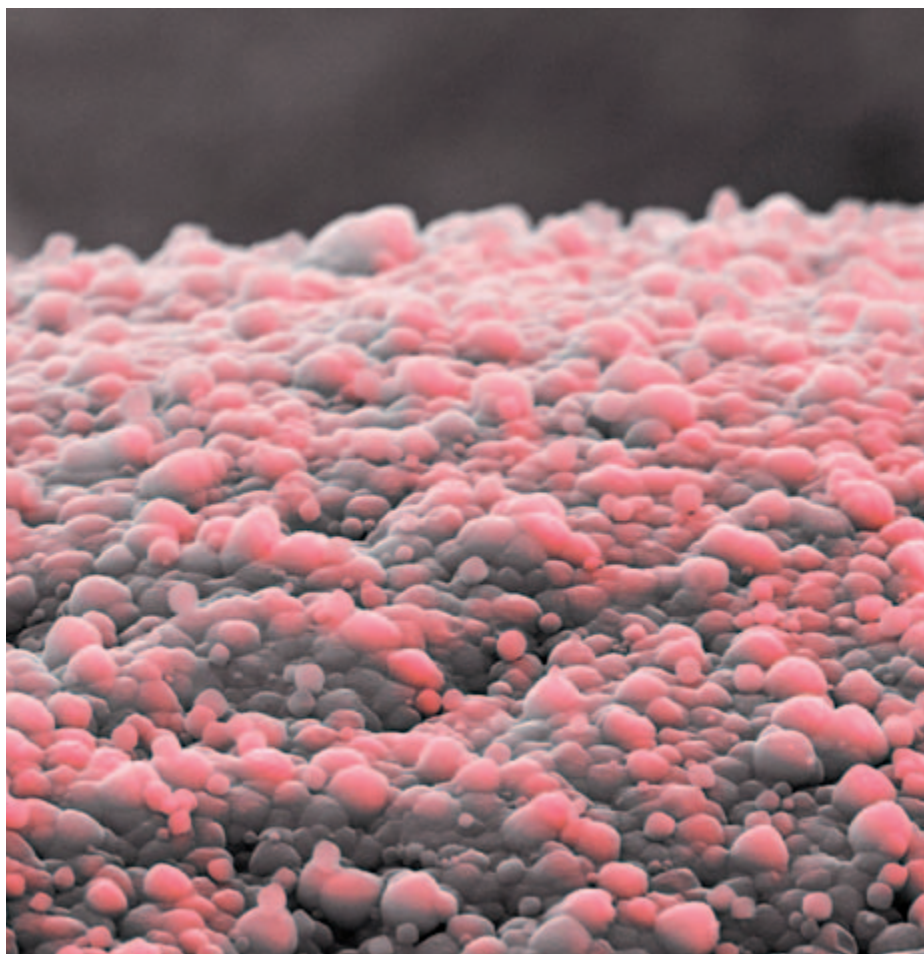
Theodor-Heuss Allee 25

60486 Frankfurt am Main

Phone: +49 (0)69 7564-452

Fax: +49 (0)69 7564-117

E-mail: [gecats@dechema.de](mailto:gecats@dechema.de)



[www.gecats.de](http://www.gecats.de)