



Catalysis – Key to a Sustainable Future

Science and Technology Roadmap
for Catalysis in the Netherlands

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Colophon

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Contents

1	Setting the Scene of the Roadmap	5
2	Approach	10
3	Fossil Raw Materials	13
4	Biomass and Renewable Resources	21
5	CO ₂ Conversion and Solar Energy Storage	29
6	Catalytic Synthesis of Bioactive Molecules	37
7	Precision Synthesis of Functional Materials	45
8	Integrated Multi-Catalyst Multi-Reactor Systems	53
9	Fundamentals and Methodology	61
10	Annexes	69
	List of contributors	70
	Background documents	71
	Abbreviations	72



Setting the Scene of the Roadmap

5

Today's society needs to prepare itself for a more healthy future with food for all and plenty of energy and resources to fuel our growing prosperity. The field of chemistry is ready to take on this global challenge. In particular, catalysis is a crucial discipline when it comes to providing the scientific and technological foundation for making cleaner, more efficient, and economically viable chemical production processes. In this document, the Dutch catalysis community presents its 2nd Science and Technology Roadmap for Catalysis for the next 20 years and describes how it will treat the feedstocks of the future, how it will use catalysis for the production of transportation fuels, bioactive molecules and materials, and how it will further integrate reactions, catalyst materials, reactors, and production processes at all length scales of importance.

In its *Horizon 2020* Framework Program, the European Union has defined **seven societal challenges** that will guide research-and-development efforts in the decades to come. Chemistry in general, and catalysis in particular, is directly relevant to most of those, e.g. in the way we design and synthesize materials for energy storage. Or in how we will re-think our production processes in a *biobased economy*, where the main source of all our chemical building blocks will no longer be fossil but biomass. Chemistry is also directly related to the way we are going to design products and processes with optimal resource efficiency, using the byproducts as secondary raw materials for other processes rather than simply creating waste like CO₂. This is a *prerequisite for a circular economy*. Furthermore, chemistry plays a pivotal role in the challenges regarding transport and health. Consider the development of new fuels and fuel cells, for example, or synthetic biology and the synthesis of bioactive molecules such as antibiotics. As over 85% of all chemical products today are produced via catalytic reactions, new developments in all fields of catalysis will have a huge impact in tackling the above-mentioned challenges.

Seven Societal Challenges in Horizon 2020

1. Climate action, environment, resource efficiency and raw materials
2. Secure, clean and efficient energy
3. Food, agriculture, marine and maritime, inland water research, Biobased Economy
4. Smart, green and integrated transport
5. Health, demographic change and wellbeing
6. Secure societies
7. Europe in a changing world – inclusive, innovative and reflective societies

In the Netherlands, the national government, environmental NGOs, trade unions, energy producing companies, chemical companies, and many other organizations agreed on *a highly ambitious Energy Initiative* in 2013. That set a target of reducing energy consumption by 100 PJ by 2020 but also ensuring a 16% share for renewables in energy production. In the long term, by 2050, the Netherlands' energy supply system should be climate neutral. Given these high ambitions and the apparent lack of a long-term strategy for achieving these goals, the government was advised to draw up an authoritative *Innovation Agenda*. Another relevant ambition was put forward by the Dutch chemical industry (VNCI) in its *Roadmap*, namely to have reduced its emission of greenhouse gases by 40% by 2030. Recent German and British Roadmaps have put forth the huge potential of catalysis as a way to reduce the energy intensity and greenhouse-gas emissions of the chemical industry. Game changers could include the use of biomass feedstocks and the production of hydrogen from renewable energy sources, as well as the direct utilization of CO₂ in chemical synthesis. These would provide new routes for making fuels and chemicals in a truly sustainable way.

These worldwide and national considerations are nicely complemented by the recent *Vision 2025 for Chemistry and Physics* within the Netherlands, developed by the Dutch chemistry and physics research community. It defines a research agenda with seven grand challenges for Dutch chemistry and physics, including *Sustainable (Bio)Chemical Process Engineering*, *Advanced Materials*, and *Energy*. For Energy, it argues that a “transition to sustainable energy conversion and storage is required due to finite reserves of fossil fuels and the impact of climate change. This transition is of such a scale that it requires extensive short- and long-term research in physics and chemistry (combined with other sciences). In the short term, new technologies will extract and convert solar energy

more directly, whereas biomass or re-use of carbon dioxide will be the key resource for many chemicals.” Catalysis, being a truly interdisciplinary research effort, is a key technology in this transition. In addition, the *Top Sector Chemistry*, as installed by the Netherlands Ministry of Economic Affairs, has realized the (economic) value of the grand challenges in this “Vision 2025”. Consequently, it selected *Chemical Conversion, Process Technology & Synthesis* and *Advanced Materials* as two of its spearheads for future developments within the Netherlands. The present Roadmap for Catalysis aims to do the groundwork for this strategic planning. It could well form the foundation for new public-private partnerships and other research activities revolving around catalysis in the Netherlands.

With a turnover of € 60 billion (8% of GDP) the chemical industry in the Netherlands is an important economic factor. Catalytic processes are of utmost importance for this industry: 85% of the chemical products are manufactured using catalysts. Also in the energy sector, e.g. in refineries, catalysts play a key role. The chemical sector aspires to grow during the next decades, and be active along the entire value chain from feedstock to end-user market. Research and development in catalysis can be a key enabler for this process. A significant contribution of sustainable bio-feedstock for the chemical industry will require robust catalytic conversion processes. New generations of catalysts will enable energy- and atom-efficient production processes. And, by successful cross-disciplinary cooperation, catalysis can contribute to new developments in materials and life sciences.

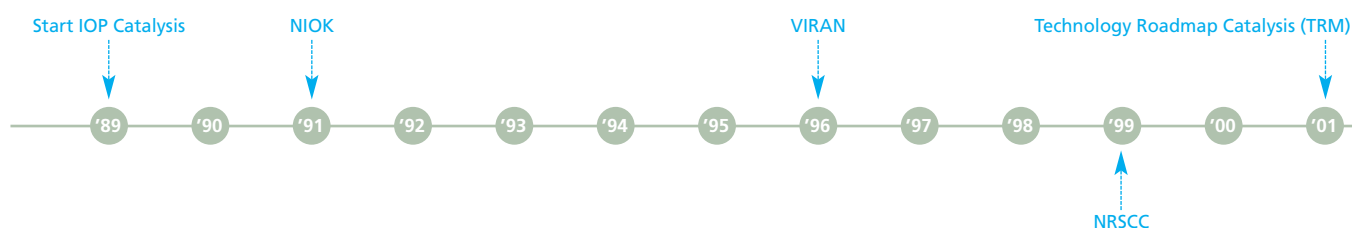
Chemistry in general – and catalysis in particular – has a rather unique position in the Netherlands, just as the Netherlands has a rather unique position in the international catalysis community. Past investments, both in academia and in industry,

have created an *excellent science and technology base* for catalysis research and development. Exemplary in this regard are the Netherlands Research School Combination Catalysis (NRSCC) and the Netherlands Institute for Catalysis Research (NIOK), with its Industrial Advisory Board, VIRAN. Together, they initiated the first Technology Roadmap Catalysis in the Netherlands in 2001. The evaluation of the previous Roadmap is summarized beneath.

Evaluation Technology Roadmap Catalysis 2001

- The Roadmap gave rise to three ACTS research programmes: IBOS, ASPECT and Sustainable Hydrogen
- The update of the Roadmap in 2006 led to the initiation of the SMARTmix programme CatchBio
- The Roadmap has increased the international visibility of the Dutch school of catalysis
- The Roadmap has strengthened the cooperation between the Dutch chemical industry and universities
- The Roadmap was highly ambitious – good progress was made but many goals were only partly achieved

The first Technology Roadmap Catalysis set an example for a number of international Roadmaps in the decade that followed. This has given what is referred to as the *Dutch school of catalysis* a reputation as a world leader in science, and the country is still home to many large chemical industries. This position at the international forefront calls for a constant influx of intellect and ideas, but also investments. The Dutch innovation ecosystem is collaborative in nature; in academia, cross-disciplinary research programs have been set up, for example between chemistry and (reactor) engineering or between chemistry and biotechnology. At the same time, and especially in the field of catalysis, the Netherlands has a strong tradition of successful public-private-partnership research programs, such as IOP Catalysis (1989–



1998), ACTS (2002–2013), and the public-private programs NIMIC and CatchBio (2008–2016). Now we need to extend this collaborative effort to include innovative SMEs, we need to strengthen already very promising research directions, and we need to expand in newly emerging research-and-technology avenues in which the Netherlands can make valuable contributions. All this forms the basis for the newly developed, and therefore second, *Science and Technology Roadmap for Catalysis*.

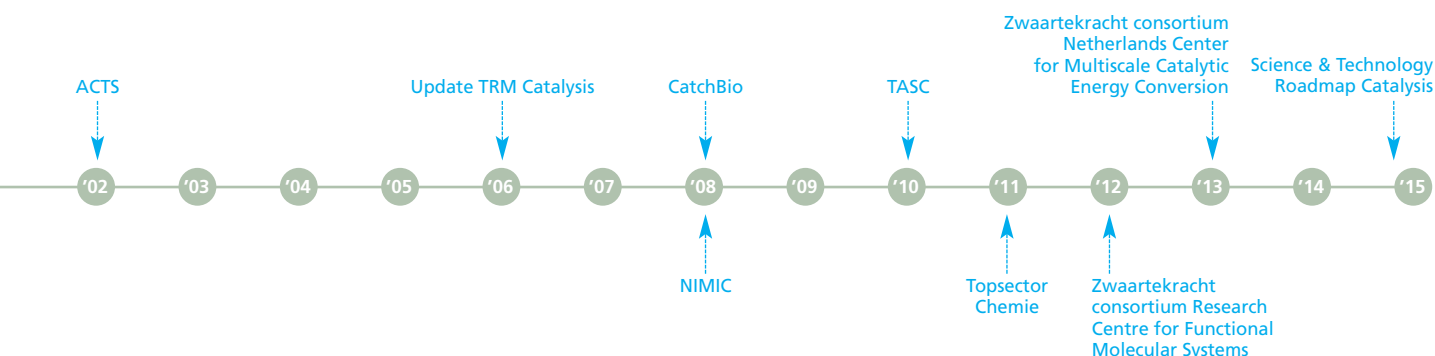
Working together, academic and industrial partners have created the present Roadmap. It presents the **current scientific and technological challenges and opportunities** for seven specific topics in catalysis in the Netherlands, describing for each topic a number of exciting **future research directions** and offering a brief outlook on the results that those may deliver. All of the proposed areas of research and the resulting products are driven by our ambition to create clean, efficient production processes that are economically viable. In biomass conversion, for example, this means that we propose to work on gaining a detailed understanding of catalysis, process technology, agriculture, and biomass production chains. And that we propose to direct our efforts to converting carbon dioxide into chemical building blocks and energy carriers using

renewable energy sources, as this is essential to cope with the negative impact of increasing atmospheric CO₂. This would clearly contribute towards tackling the challenges the EU faces in terms of clean energy as well as resource efficiency. The example also nicely demonstrates the integrated approach in which different (sub-) disciplines all contribute to the same challenge. The other topics in this Roadmap relate to the societal challenges in a similar way. They include fossil resources (Chapter 3), the catalytic synthesis of bioactive molecules and functional materials (Chapters 6 and 7), the integration of multi-catalyst, multi-reactor systems (Chapter 8), and related experimental and theoretical methods (Chapter 9).

Three-stage systems catalysis approach

1. Fundamental understanding of the catalytic system
2. Predictive theoretical multiscale model of the catalytic system
3. Design of knowledge-based synthesis strategies that can be controlled that can be controlled at the different length scales required

Across all topics, we have chosen to apply a **three stage systems-catalysis approach** in which we



consider the catalytic process from the nanometer or atomic detail of the reaction to the meter scale of the reactor as a whole. A fundamental understanding of the reaction in real systems under process conditions is acquired through sophisticated analytics, e.g. operando microscopy and spectroscopy. This is then followed by the development of a predictive theoretical model that spans all relevant length scales and contains sufficiently detailed chemical descriptors of the catalytic reaction and related reaction steps. From these descriptors a knowledge-based synthesis strategy is developed for the desired molecule or material.

Unique qualities of Dutch school of catalysis

1. Infrastructure in academia and industry is in place
2. Industrial and academic groups work close together, geographically and culturally
3. Excellent track record in collaborative research
4. Excellent level of academic education

The key to such an integrated systems-catalysis approach is the ability and willingness to collaborate between various disciplines and between academic and industrial research and

development. The Netherlands is uniquely positioned to make this approach work: most of the infrastructure is already in place, industrial and academic groups work closely together (both geographically and culturally), and they have an excellent track record in terms of collaborative research-and-development efforts.

Finally, the historically strong position of Dutch catalysis coincides with an excellent level of integrated chemical education in the fields of catalysis and process development. Many internationally top-class students are attracted at various educational stages (MSc, PhD and PD) to the top groups at Dutch universities, which as a result have been able to deliver many successful researchers to academia and industry. This education could be enriched by instilling knowledge of additional fields like intellectual property and marketing. The present structures we have in the Netherlands for integrating all aspects of catalysis in teaching and research are unique, and need to be nurtured and strengthened.

2

Approach



Aim

Since 2001, the year in which the previous Roadmap was presented, the world has undergone significant changes in terms of important societal issues, the economic situation, the structure of research funding and the interests/strategy of industry (including the chemical industry) in the Netherlands. In 2013, together with the Top Sector Chemistry, the Dutch catalysis community, represented by NIOK and VIRAN, decided to create a new *Science and Technology Roadmap for Catalysis*, which would build on this changed situation. The aim of this report is to develop a vision of catalysis research in the Netherlands for the next 10 to 20 years.

Process

In order to realize this new Science and Technology Roadmap for Catalysis 2013, NIOK and VIRAN appointed a core team of scientists from academia and industry for developing the Roadmap. The core team was supported by a project manager, a process manager, and the NIOK/VIRAN office. The names of the members of the core team and the support team can be found in Annex 1 of this Roadmap.

During the first stage in the development of the Roadmap, the core team determined the criteria to be used in identifying which topics the Dutch catalysis community should work on in the coming years. The criteria were as follows:

- The topics should describe exciting new directions for world-class research that will help to solve a current technological and/or societal challenge and should fit in with the strengths and expertise currently present in catalysis in the Netherlands;
- The topics should be driven by the ambition to create clean, efficient production processes or products that are economically viable.

In addition, the core team determined that the Roadmap as a whole should help to strengthen the Dutch catalysis community, lead to a greater integration of the heterogeneous catalysis, homogeneous catalysis and biocatalysis community, provide opportunities to start collaborations with other research fields (e.g. process technology, biotechnology, physics) and help the community to stay at the international forefront.

In January 2014, a workshop with 65 participants (see Annex 1) served as the kick-off for the discussions with the catalysis community. The participants discussed the new trends in science, the strengths and weaknesses of the Dutch academic catalysis field, the major challenges facing society in the coming years and what catalysis can contribute to help solve those issues. In addition, they discussed the opportunities for collaborating with other fields of science to maximize the impact of Dutch catalysis research. Based on this round of consultations the core team concluded that there was consensus on seven research topics to be included in the Roadmap: Fossil Raw Materials, Biomass and Renewable Resources, CO₂ Conversion and Solar Energy Storage, Catalytic Synthesis of Bioactive Molecules, Precision Synthesis of Functional Materials, Integrated Multi-Catalyst Multi-Reactor Systems, and Fundamentals and Methodology. For each topic the core team then developed a position paper. These were discussed and reviewed by experts in the field. The results are presented in Chapters 3-9 of this Roadmap. Each chapter presents a brief description of the state of the art and current challenges and opportunities for catalysis. Subsequently, the specifics of the Dutch situation are highlighted. From this, a selected number of research areas are derived with a set of related deliverables.



Fossil Raw Materials

3

13

The conversion of fossil raw materials to fuels and chemicals will remain important for at least the decades to come. In view of the enormous volumes of converted materials, even minor improvements will have a substantial impact. In view of geopolitical developments such as the recent use of shale oil and shale gas, this market is a highly dynamic one. We will need new catalysts for the activation of methane but also other C_1 carbon sources, including CO_2 , as well as more flexible and robust catalysts and processes for the conversion and cleanup of heavy feedstocks. We also need to understand the processes of catalyst deactivation and to replace scarce raw materials, such as noble metals, for catalyst manufacture.



Status & Challenges

Current Situation

The use of catalysis in support of the conversion of fossil fuels may appear to be relatively mature, yet there are clear developments that require fundamental improvements in this field. The amount of crude oil refined every day worldwide amounts to about 85 million barrels. This implies that even the smallest improvements in selectivity or effectiveness in the processes used translate to a significant impact.

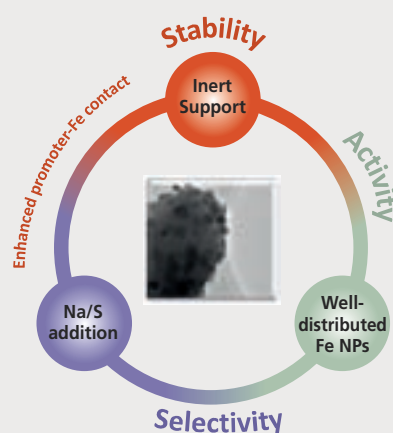
Solid, liquid, or gaseous fossil raw materials are, and will remain, the main sources of raw materials for the production of transportation fuels and chemicals in the foreseeable future. Although oil and gas production may peak during the next two decades that will not diminish their role. Especially gas (methane) will become more important, as explained below in more detail. The quality of crude oil will decline, and disadvantageous crudes will become more attractive for conversion. This will require more stable catalysts with improved resistance to poisons. Gas, and particularly shale gas, will become more important in the near future.

Due to its local availability, shale gas is likely to disrupt current economic balances. Since shale gas is relatively light and paraffinic, its use as a cracking feedstock may lead to a shortage in olefins like propylene, butadiene, and C_4+ molecules, specifically aromatics, see also the challenges paragraph in Chapter 4 Biomass and Renewable Resources. Other sources of methane, such as deep-sea hydrates or methane from permafrost, could become relevant later on. Furthermore local sources of methane from the anaerobic conversion of biomass may become relevant from a raw-materials standpoint (valorization of fugitive emissions). Coal may also become more important, especially in China, and will most likely be available for a very long period.

Oil- and gas-producing nations will claim a larger share of the value chain, and as a result, the production of base chemicals will move towards these countries. Smaller northwest European refineries and petrochemical complexes will likely become less economically feasible, so capacity will be replaced by larger complexes in Asia and the Middle East. The present oil- and gas-based processes are at close to peak efficiency, but future legislation and for instance new engine designs may

Lower olefins directly from synthesis gas

Hirsa Torres Galves from the group of Krijn de Jong in Utrecht (Torres, H.M., et al. , Science 335 (2012) 835-838) designed supported iron nanoparticles as catalysts for the production of lower olefins, and found effects of both particle size as well as promoter atoms. The catalysts displayed a remarkable selectivity towards lower olefins in Fischer-Tropsch synthesis. The work was performed in the ACTS-ASPECT-program.



require different designs for future refineries to enable more flexibility. When a shift to new energy carriers (hydrogen, electrons, or new chemical energy carriers) is eventually made, a new infrastructure will have to be developed. That, in turn, will mark the beginning of a new S-curve, with plenty of room for innovation, which is outside of the scope of this report, but even for conventional energy carriers based on renewable resources, the early part of the supply chain will have to be (re-)developed. The later stages of the infrastructural chain can remain more or less the same. Marine transportation fuels are the last remaining fossil-based, high-sulfur fuels, and these fuels will also require treatment to decrease sulfur content. Researchers are working on a catalytic solution for this problem.

The subject of Fossil Raw Material conversion was addressed in Cluster I and Cluster II of the 2001 Technology Roadmap. In Cluster I, a broad program on hydrogen was selected for execution, and subjects like CO₂ sequestration were not widely examined. In Cluster II, mainly directed to the conversion of fossil raw materials to bulk chemicals, the ASPECT program was established. This successful program examined conversion to bulk chemicals in over 75 individual projects, 110 scientific papers, and 3 patent applications.

Challenges

The main challenges in replacing liquid fossil raw materials by gas or coal are the initial C-H activation and the thorough understanding of carbon-carbon coupling reactions. The same holds for a number of routes based on renewable resources. C₁ chemistry as a whole is a major theme, whether it be methane or methanol based, carbon monoxide based (Fischer-Tropsch) or even carbon dioxide based. Fischer-Tropsch synthesis, especially from coal, will become more important in China. A similar observation holds for the large

interest in methanol to olefins (MTO) in China. Process integration, separation and functionalization are relevant elements to improve on the present body of knowledge.

In the short term, the availability of shale gas may negatively influence the availability of C₄-C₆ building blocks (especially butadiene), which would result in a demand for oligomerization catalysts and processes starting from e.g. ethylene or even ethane. At the same time, there will be an increased need for hydrogenation and dehydrogenation processes to balance the supply of and need for smaller hydrocarbon building blocks.

Oxidative Coupling of Methane (OCM) has been studied extensively in the past as a way to activate methane and produce larger molecules, but the selectivity and yield are still not high enough to be sufficiently competitive with e.g. steam cracking because of the reactivity of the products towards oxygen. This research line does not seem to offer opportunities, and should best be abandoned. However, the research has yielded valuable insights with respect to the need for intimate coupling between catalyst and process, for instance in catalytically active membranes, which should be taken into account. This implies that research on integrated systems is a promising field. In general, flexible integrated processes for the conversion of gas to fuels and chemicals are required to be able to respond to fast-changing feedstock availability. One could think of flexible processes for converting smaller molecules to larger ones, the dehydrogenation or functionalization of alkanes, or an improved process for catalytic steam cracking with added product flexibility. Although the latter is a tough challenge, steam cracking is one of the processes that would benefit most from catalysis, especially from an energy standpoint, through lower temperature and through selectivity control.

The use of **diesel as a transportation fuel** is becoming more important in the US. In the present situation, gasoline is transported from Europe to the US, and diesel is shipped back. With the increasing demand for diesel in the US, this cannot be maintained, which is creating an imbalance in refinery outputs. This generates the need for new processes that have a higher selectivity to diesel at the cost of gasoline, such as diesel-selective Fluid Catalytic Cracking (FCC) or hydrocracking.

For the conversion of coal, improved catalytic processes like hydrogenation, sulfur resistant gasification, and methods for the selective conversion of aromatics from coal tar are relevant.

In conventional processes, a lot of money (both investment costs and running costs) is spent on separation. **Avoiding separation steps**, either by designing catalysts and reactors that can handle complex mixtures of raw materials or by coupling catalytic solutions with separation technology in the process, would be very worthwhile. We could think of the oligomerization of untreated shale gas, olefinicity changes in mixtures of alkanes and alkenes, etc. It would also be interesting to look at ways of introducing energy only at the catalytic site, i.e. without heating up the whole medium.

Opportunities for Catalysis

The overviews presented in the previous two sections provide plenty of opportunities for catalysis. In view of the increasing effort required for the conversion of ever-heavier and more disadvantageous crudes, **improved catalysts for heavy-oil conversion** are needed. These will require increased porosity to avoid mass transfer limitations, and at the same time they will need to be more resistant to poisoning and deactivation. There may be some options for homogeneous solutions in this field, as evidenced by the ENI Slurry Technology process, for example, in which

dispersed catalysts are used in the hydroconversion of heavy feedstocks.

Related to this, the **cleanup of feedstocks** will become more important. Low levels of impurities can travel through the installations and show up in unexpected and unwanted places. Apart from the obvious impurities, sulfur and nitrogen, also antimony, arsenic and mercury are important in this respect.

Fundamental research on catalyst fouling, deactivation, feedstock variability, mechanical deactivation, breakthrough curves, roles of contaminants in catalyst stability, etc., is required. This also implies a challenge in analytical research, where new (micro-) spectroscopic techniques can be used to increase our understanding of catalysts (and their deactivation) on all length scales, see also the challenges in Chapter 9 Fundamentals and Methodology. These techniques can also increase our fundamental understanding of the effect of promoters. Apart from feedstock cleanup, the **cleanup of waste streams**, i.e. environmental catalysis, is a still increasingly important field. Catalysts and processes for the in situ (pre-) treatment of crudes will improve transportability and recoverability.

Flexible systems and processes would allow for a rapid response to the changing availability of feedstock, for instance in catalytic steam cracking as described above. Current large-scale processes target steady state operation, and transients lead to considerable off-spec production. More flexible systems and understanding of the transient states would be welcome, see also the challenges paragraph in Chapter 8 Integrated Multi-Catalyst Multi-Reactor Systems.

Steam cracking is one of the most energy-intensive processes in current petrochemical complexes. Developing a more energy-efficient process with an

improved selectivity to the desired products like ethylene would be a great opportunity for catalysis. The scale of operations and multipliers in refinery and petrochemistry are so large that even relatively small improvements will have a large impact, also on CO₂ emission.

Dutch Strengths in Fossil Raw Materials

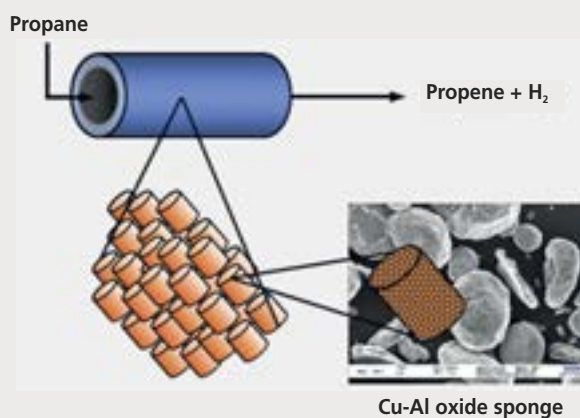
The Netherlands does not have access to a large fossil fuel deposit, except from natural gas and presently unused coal. The development of shale gas is still under debate. Historically, Dutch research has made considerable contributions to the conversion of coals and methane. As the world around us is shifting to the use of C₁-sources (methane and coal) we believe the research on methods for gas conversion and carbon-carbon coupling should be intensified.

The Netherlands is world-leading in catalysis because it has high-level groups focusing on characterization, understanding and application, as well as a large catalyst manufacturing industry. Industrial research has partially left application research, and the gap has not been completely filled by academia. Therefore, future strategy should focus on maintaining the very good interaction between industry and academia.

The Dutch catalysis community also has a strong history when it comes to the fundamental science behind catalyst preparation. The cooperation between industry and academia in this field should be given the opportunity to flourish. The combination of theory, high-resolution analysis, and 3D atomic-precision catalyst preparation for making tailored, structured systems provides a set of tools for better understanding of the fundamentals of catalyst preparation. This understanding will fill the gap between 2D models and practice.

No Platinum needed

Jana Schäferhans, working with Prof. Gadi Rothenberg in Amsterdam, developed a Cu–Al bimetallic oxide “sponge” that outperforms conventional noble metal catalysts in propane dehydrogenation. The catalyst gives higher conversions even when the temperature is 200 °C lower than the optimal temperature for the benchmark Pt–Sn/Al₂O₃ catalyst (Chem. Eur. J. 2011, 17, 12254–12256).



Yet another major strength of the Dutch school of catalysis is its **integration of catalysis and process design, especially in process intensification**. This can be used to create the desired flexibility in feedstocks and routes, for instance by coupling modular (micro) reactor arrays. This integration of catalyst research with process design, which translates to a multi-scale, multi-discipline approach to problems, is highly desirable.

The **conversion of heavier feedstocks** is a research field that is strong in the Netherlands, both in industry and academia, with players such as Albemarle, Shell and BASF as catalyst producers as well as academic research groups in e.g. Delft, Eindhoven and Utrecht. This research needs to deliver catalysts and systems that can help bridge the ever-widening gap between (heavier and dirtier) feedstocks and (cleaner) products. This requires improved hydrogenation, which in turn requires a low-cost and abundant source of hydrogen, cracking of lower-quality feedstocks, resistance to impurities and poisons, and the ability to selectively crack and induce ring opening in (poly)aromatic systems.

Research Areas & Deliverables

Areas of Research

Based on the above discussion and balancing of the needs and strengths, four priority areas of catalysis research have been identified. It should be emphasized that the scale of operation and the multipliers in this field (refinery and petrochemistry) are so large that even relatively small improvements will have a large impact.

First, the development of **flexible processes for converting molecules** will become even more important than it currently is. At one end

of the spectrum, there are reactions like (de)hydrogenation and the functionalization of alkanes, methods for C-C-coupling and C₂-oligomerization starting from CO/H₂, CH₄, C₂H₄, C₂H₆ or CH₃OH, for instance for the production of C₂-C₄ olefins with a focus on methane as the starting material. The integration of catalyst and process design will be instrumental in creating the desired flexibility. At the other end of the spectrum, there is the design of robust catalysts and systems for heavy oil conversion that can bridge the widening gap between (heavier and dirtier) feedstocks and (cleaner) products are required. The effects of catalyst-structural parameters and chemistry (including promoters) on the stability and deactivation of catalysts, and the effects of poisons are crucial in this respect.

Secondly, developing a **more energy-efficient and selective catalytic modification of steam cracking**, with less CO₂ production, would be a great challenge for catalysis.

The third area comprises research into ways of **activating CO₂**. These are discussed in Chapter 5 CO₂ Conversion and Solar Energy Storage.

A fourth area is research directed towards **filling the gap between 2D models and practice** by an improved understanding of the fundamentals of catalyst preparation through the combination of theory, high-resolution analysis, and 3D atomic-precision catalyst preparation. The design and understanding of catalysts in refinery and petrochemistry typically calls for (kinetic and molecular) models spanning several orders of magnitude in length scales (from nanometers in describing surface reactions, to meters in describing bed packing, hydrodynamics and strength). We will need to bridge the temperature and pressure gap in spectroscopy and microscopy, and we will need to study real systems rather than model systems. This area is further detailed in Chapter 9 Fundamentals

and Methodology. Just as fossil fuels are finite, some constituents of catalysts, such as noble metals, several transition metals and even phosphorous, are becoming increasingly scarce. Research lines investigating the application of more abundant elements as active components in catalysts are very important.

Deliverables in 10-20 years

- Integrated flexible processes and catalysts for efficient carbon coupling, allowing rapid response to changes both in raw material and energy input, as well as product functionalization. This will allow for the design of easily adaptable refinery complexes that can handle a greater variety of feedstocks;
- Robust, stable and efficient catalysts and processes for conversion of heavier and dirtier feedstocks and coal, as well as catalysts and processes for in situ (or at least pre-transport) improvement of crude quality;
- Flexible and efficient catalytic systems or processes to allow rapid response to changing feedstock availability. This applies especially when European refiners apply mixes of biomass-derived feedstocks and conventional petroleum fractions;
- Optimized catalysts based on non-precious metals that can replace noble metals and heavy transition metals that are linked to health or environmental concerns.



Biomass and Renewable Resources

21

A detailed understanding of the fundamentals of the various forms of catalysis, process technology, agriculture, and biomass production chains is essential if we are to arrive at an economically viable and sustainable biobased economy. Catalysis is key in those processes. The main challenges for catalysis involving biomass and renewable resources are 1) selectivity, i.e. how to convert the complex biomass mixture to the target molecules -either drop-in or new molecules- in as few steps as possible thus preventing intermediate separations and 2) stability, i.e. how to achieve a catalyst that can handle “poisons” present in the biomass and that survives the conditions needed to convert biomass.

Status & Challenges

Current Situation

In the first Roadmap Catalysis biomass was mentioned as one of the potential feedstocks to make fuels and chemicals. It was stated that “Biomass is increasingly being used for power generation and from a fundamental point of view it should be considered for the production of chemicals.” (Cluster II - p47). Since then the appreciation of biomass as a feedstock became more prominent since it is a renewable feedstock and therefore contributes significantly to sustainability.

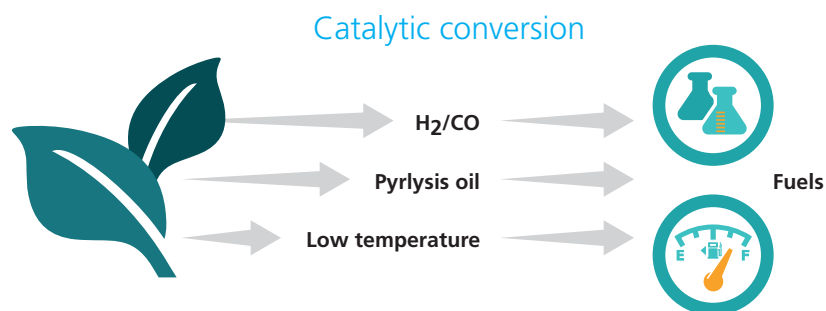
All biomass is highly heterogeneous and generally contains a fraction to be used for the production of food and feed, as well as residues and side products that are potential feedstock for materials, chemicals, fuels, and energy. For materials, chemicals, energy, and fuels production, the five main classes of compounds in the biomass that can be used are cellulose, hemicellulose, lignin, lipids, and proteins.

To valorize biomass three routes are envisioned, all of which contain catalytic steps i.e., the syngas route, the pyrolysis route, and the low temperature route (see Figure 4.1). The first two routes break down the biomass either to syngas (route 1) or bio-oil (route 2), after which the further conversion is similar to processes developed for fossil feedstocks.

However, these processes have a special edge related to catalyst stability. The third route maintains as much as possible the functionalities present in the biomass. The latter route needs significant research input, also from catalysis, to convert the complex biomass mixture to desired molecules. Yet, since the biomass is highly functionalized, this route is very promising for making (bulk) chemicals.

Up till now, the commercial valorization of biomass to fuel, chemicals, and materials has been narrowly limited to a few value chains, and broad commercialization has yet to come. So far, commercial applications include the fermentation of sugar to ethanol, lactic acid and succinic acid, the valorization of vegetable oils and the modification and use of natural fibers. Hence, we are often at the stage of explorative research, gaining knowledge on how to selectively convert these resource classes. More often than not, model or pure compounds are used to develop new catalysts for biomass conversion, for example in the Dutch private partnership CatchBio (Catalysis for Sustainable Chemicals from Biomass). In the last stage of CatchBio, more attention is being given to the conversion of real complex feedstocks, a step that requires further attention in order to arrive at an economically viable use of biomass.

Figure 4.1
Three catalytic
routes to valorize
biomass



An initial set of platform molecules that can be generated from biomass, in particular from sugars, has been defined. However, this set does not yet cover as wide a range as that known for fossil resources. No preferred feedstock-product combinations have been developed to maturity, which indicates that much explorative work is still needed.

Challenges

If we concentrate on the products higher up in the value chain, i.e. chemicals and materials, using biomass as a resource brings up a couple of specific topics. Bulk chemicals are facing the emergence of cheap shale gas, which offers an opportunity for lower olefins (particularly ethene), but does not easily deliver heavier chemicals such as C₄+ and aromatics. Renewables may present an attractive alternative feedstock for the production of such heavier chemicals in this case. With respect to the production of functional chemicals, the clear advantage of biomass is that it contains a wealth of functionalized molecules. In the production of (performance) materials, a main driver for the use of renewable resources is the customer-based need for sustainable production at competitive costs. The conversion of only a limited number of components of the biomass does not lead to products at competitive costs. For example, cellulose as well as hemicellulose and lignin (i.e. lignocellulose) are affordable but prohibitive to upgrade, because 1) fractionation and gasification is expensive and 2) biocrude is difficult to valorize. In addition, lignin depolymerization is difficult and leads to a complex product mixture. Pure and well defined sugars made from the cellulose fractions are costly to produce. Upgrading them is also challenging, mainly because this requires either multiple conversion steps (typical of chemocatalysis) or a difficult product recovery from dilute solution (typical of biocatalysis). Other drawbacks are that upgrading proceeds with moderate selectivity (chemocatalysis) or with low volumetric productivity (biocatalysis). Currently,

the valorization of the lipid fraction of the biomass is a challenge which is related to the high production costs of the products. Typically, until now deoxygenation reactions with the use of costly hydrogen are used to upgrade the lipid fraction. Therefore production routes based on fossil feedstock are more competitive thus new catalytic routes for lipid upgrading are needed to make the use of lipids competitive. Proteins and their building blocks, the amino acids (only the non-essential ones should be used for chemicals), are potentially suitable for bulk chemicals. However, cost-effective isolation and selective conversion are still in their inception phase. Therefore an integrated biorefinery approach is needed to valorize all components in the biomass at their highest value. Please note that not only value but also market volume should be taken into account. If we are to meet these challenges, the integration of expertise is imperative – not only within the chemistry and process-technology disciplines, but also in a much broader sense.

So far we have discussed the technological issues, including the key role for catalysis. However, integrative thinking with respect to biomass production is also essential. To determine which biomass is available and how we can modify that biomass in such a way that feed, food, chemicals and fuels can all be prepared in an economical way, input from the agricultural side is needed. In addition, since biomass suffers from seasonal variation, the issues of transport and storage also need to be addressed.

For catalysis, when dealing with the catalytic conversion of biomass as a renewable resource, three main challenges stand out:

1. developing stable catalysts,
2. going towards more selective reactions, and
3. integrating catalysis with separation.

These challenges are not uncommon to catalysis, but they have a specific edge with respect to renewable resources.

Opportunities for Catalysis

The use of biobased resources introduces new requirements for the catalysts used. As for chemical catalysts, **stability** is a major issue, as they should function in a liquid (slurry), often an aqueous or acidic environment, and they should be resistant to the relatively high ash content, which can poison the catalyst. Moreover coke formation resulting in catalyst fouling should be prevented. Thus studies of catalytic behavior under both model and real conditions are essential. Concerning biocatalysts, the use of whole cells (in which the enzyme/biocatalyst is incorporated) is desirable if we want to use them in a (one-pot) biotechnological environment or in a modular set-up operating in tandem or cascade mode. The transport of the reactant and/or products into and out of the cell is still a challenge and offers opportunities for catalyst development. In the downstream processes the applied catalysts have to tolerate the side products

of the upstream processes when one wants to omit (expensive) intermediate product separation. Finally, the new catalysts preferably contain only cheap and widely available elements.

Going towards **more reactant selectivity** presents a specific challenge for biobased conversions, as crude biobased feedstocks are generally heterogeneous in nature or at least multifunctional, e.g. purified carbohydrates. Their composition will vary depending on location, time of the year and production methods. Moreover, the advantage of a biomass feedstock, i.e. a feedstock containing complex and overfunctionalized molecules, can only be used to its full potential if we can convert these molecules selectively. Developing redox neutral reactions is beneficial since the use of (expensive) hydrogen can then be prevented.

Cascading multiple conversion reactions and separation steps could be an option to find economically viable process routes. The **integration of chemocatalysis with industrial biotechnology approaches** is a promising option in the design of a reaction cascade, as is the option to combine

Green bottles

Avantium's YXY technology makes it possible to create 100% green and 100% recyclable plastics that can compete on price and performance with today's plastics such as PET. Avantium is actively working to develop PEF bottles for water, soft drinks, food, cosmetics and detergents. In addition, the company is working on PEF fibers for textiles and carpets, PEF films and PEF thermoforming applications.

<http://avantium.com/yxy/YXY-technology.html>



various types of resources, i.e. not only biomass, but also fossil and CO₂. Specifically for biorenewables, the integration of length scales of the process and corresponding logistics is a challenge, e.g. in the development of local, small-scale production processes.

When stable and poison tolerant catalysts and catalytic process are developed, the range of available feedstocks for making products (chemicals, fuels) desired by society becomes significantly wider. For example, waste water which still contains organic matter can be used as feedstock. A typical example is the use of waste water containing volatile fatty acids (VFAs). These VFAs can be converted by micro-organisms to polyhydroxyalkanoates (PHAs). PHAs as such can be used as polymers, though their properties have to be improved. Alternatively, they can be used as feedstock for the production of bulk chemicals by chemocatalytic processes. Paques, a Dutch company specialized in integrated water and gas treatment, is very successful in this area. In an alternative route short VFAs can be converted by micro-organisms to longer VFAs which can be used as feedstock for chemicals and fuels production. Chaincraft, a recently founded innovative SME, has developed breakthrough technology to elongate short VFAs. These examples show that biocatalytic conversions and chemocatalytic conversions can go hand in hand, demonstrating that waste streams can be utilized to widen the feedstock scope.

Dutch Strengths in Biomass & Renewable Resources

Focusing on renewable resources as one of the key areas in catalysis, the Netherlands will build on its existing and recently developed strengths that are outlined below. Internationally renowned academic

expertise in agriculture, i.e. production of biomass, is present at Wageningen University that is now also a member of NIOK. This presents a clear strength which ties the agricultural sector, a major partner in the Topsector Agrifood, closer to chemistry in general and catalysis in particular. Chemocatalytic biomass conversion is a topic of research at all universities united in NIOK, e.g. pyrolysis research at the University of Twente and University of Groningen as well the company Biomass Technology Group, and the work on lignocellulose to produce sugars at Eindhoven University of Technology.

As a concept, the *biobased economy* is widely recognized and supported. Catalysis and industrial biotechnology are key technologies in the biobased economy. A large number of initiatives have been deployed to develop this field in the Netherlands, such as the public-private partnership programs CatchBio, BE-Basic, the Carbohydrate Competence Centre, and the Protein Competence Centre. Both academia and industry are actively involved in all these programs. The aggregate budget of these four programs totals around M€ 200, half of which has contributed by companies and academic institutes and the other half by the government (at the national, provincial or municipal level). Other initiatives, such as the Biobased Delta in the southwest of the Netherlands, InSciTe in Limburg, and the Green Campus and the BioProcessFacility in Delft all represent excellent examples of initiatives in which industry, academia and government all collaborate closely. Each of these initiatives in fact builds on a broader basis of expertise in conversion technology and catalysis in general, for which the Dutch school of catalysis is known for more than 50 years.

In terms of logistics and infrastructure, the fact that the Rotterdam mainport is a major hub for feedstock transportation across Europe means that the availability of renewable feedstocks is not as big

an issue as it may seem considering the small amount of land area that is available for renewable feedstock production in the Netherlands. The presence of large oil refineries in the Rotterdam mainport is a unique bonus for Dutch horticulture. The refinery byproduct CO_2 is transported to the greenhouses in the western part of the country, where it is used as a resource for plant growth.

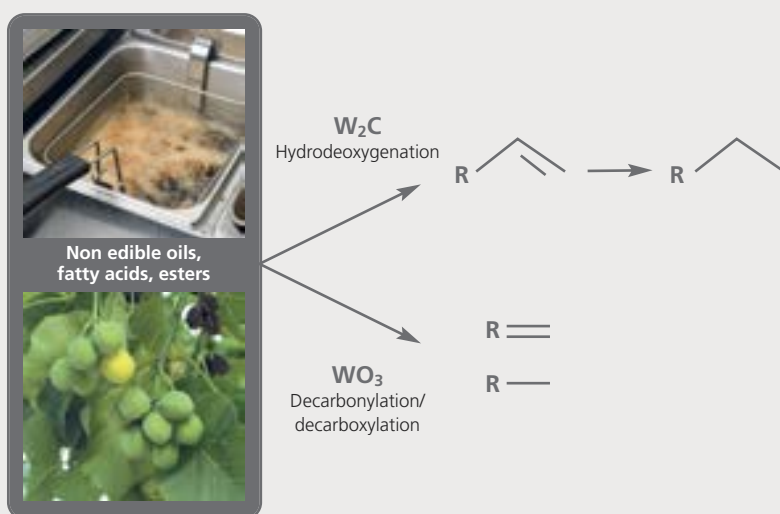
Research Areas & Deliverables

Areas of Research

To address the three catalytic challenges in the development of a mature **biobased economy** - stability, selectivity, and integration- seven areas of research are defined:

- understand and control the **reaction mechanisms and the catalyst functions** such as hydrogenation, and acid/base-functions, for operation in water. This will aid the development of stable and selective catalysts;
- understand and control the **catalyst selectivity**, both chemoselectivity as well as regioselectivity for overfunctionalized feedstock, as this will lead to fewer byproducts and thus a more efficient process in general;
- understand and control the **catalyst stability** to overcome typical issues with destruction, fouling, or poisoning of the catalyst in order to develop an effective process;
- **activate biomass**, i.e. make the solid biomass suitable for further conversion. By proper

Tungsten-based catalysts for deoxygenation of triglyceride-based feedstocks



Rob Gosselink, working with Prof. Bitter Utrecht/ Wageningen, (Gosselink, R. W, et al., Angew. Chem. 125: (2013), 5193–5196), demonstrated the use of tungsten-based catalysts for the deoxygenation of triglyceride-based feedstocks. Changes in a (pre)treatment procedure are shown to control catalyst selectivity 1) to decarboxylation/ decarbonylation products i.e. the carbon chain in the products is one carbon atom shorter as in the feedstock or 2) to hydrodeoxygenation i.e. the carbon chain in product is has the same length as in the feedstock. In addition high yields of unsaturated products even in the presence of hydrogen can be achieved.

activation of the biomass downstream processing becomes more facile i.e. more selective process can be developed. Input from e.g. plant sciences is essential;

- develop new catalytic routes to new molecules with predefined properties. The new molecules need to be defined in collaboration with industrial partners;
- integrate the catalysis with separation technology in order to mitigate the challenges presented by high dilution, feed contaminants/heterogeneity or abundant byproducts;
- integrate different forms of catalysis to arrive at more efficient product formation.

Research in all these directions will benefit from an inclusive approach in which biocatalysis, homogeneous catalysis and heterogeneous catalysis are considered along with other scientific disciplines and, if beneficial, integrated for the development of efficient, low-cost conversions. Moreover, we need to consider the options for the integration of fossil and renewable feedstock for an optimized product mix, i.e. one with the highest added value. This means establishing which resource (or mix of resources) can best be used in a specific production chain.

Of course, issues with catalysis in general – such as the replacement of scarce and expensive metals in catalysts and the development of dedicated computational tools for modeling experimental results and for data handling – apply to renewables resources just the same, see also the research areas paragraph in Chapter 9 Fundamentals and Methodology.

Deliverables in 10-20 years

The Top Sector Chemistry has set the ambition for the Netherlands to be world-leading in green chemistry by 2050. More specifically for this Roadmap, a highly ambitious deliverable in 20 years' time will be the full use of industrial and agricultural waste streams as a resource in the production of chemicals and fuels. If we distinguish deliverables per type of resource, i.e. (hemi)cellulose, lignin, lipids and proteins, we come up with four deliverables in 10 to 20 years' time.

The biomass feedstock is complex and variable by nature. The main challenge is to convert this complex feedstock into tailored products. To arrive at that point the deliverables will be:

- new catalysts with improved reactant selectivity, i.e. the catalyst converts only the desired molecules from the feedstock to the desired products. Some of the (new) products still need to be defined;
- understanding factors that determine the stability of catalysts under relevant biomass conversion conditions, i.e. stability in water, with respect to poisons and coke formation;
- integrated systems, i.e. integrating the unit operations (biomass activation, conversion separations) which make the overall process robust and cost effective;
- integrated scientific knowledge by combining different areas e.g., plant sciences and catalysis.



CO₂ Conversion and Solar Energy Storage

29

The conversion of carbon dioxide into energy carriers using renewable energy sources is essential in order to cope with the negative impact of increasing atmospheric CO₂. It would also solve the problem of storage of excess renewable energy. In the short term, better catalysts for electrolyzers need to be developed. A sustainable solution to the energy challenge involves the development of cheap photocatalytic materials and their integration into solar-to-hydrogen device with an efficiency of at least 20%. Together with catalytic technology for chemicals production from CO₂, such devices could vastly contribute to the realization of a more carbon-neutral chemical industry in the decades to come.

Status & Challenges

Current Situation

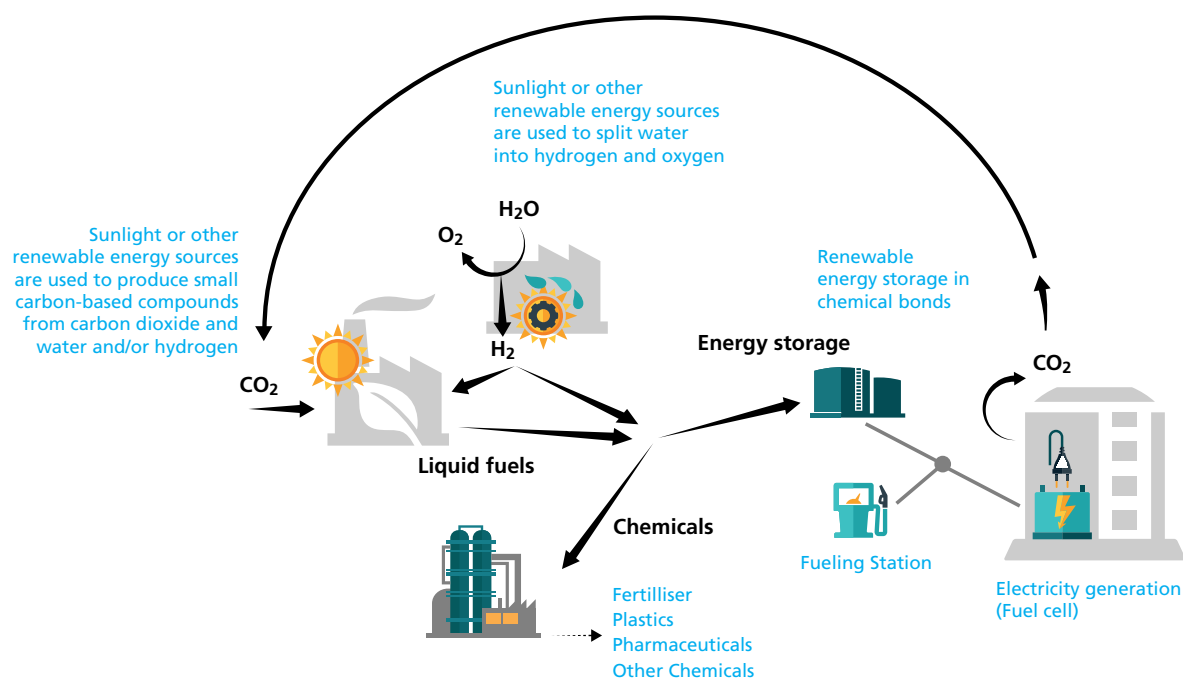
The annual anthropic emissions of carbon dioxide, deriving from combustion of coal, oil, and gas, currently amount to about 30 Gt and are expected to grow substantially in the coming decades. Given the impact of CO₂ emissions on the global climate, several strategies can be considered to **reduce fossil-carbon consumption**. Higher efficiency in electric-energy production from conventional resources may contribute to this goal, as will a more efficient use of energy. Another strategy under investigation is carbon capture and sequestration (CCS), because of its large potential for CO₂ storage. The use of renewable energy sources such as solar and wind is currently being given great attention in connection with the production of electric energy. In particular, photovoltaic (PV) cell technology is expected to contribute significantly towards replacing fossil fuels in the generation of electricity in the coming decade. As such, the direct conversion of solar energy was identified as a long term goal in the previous Catalysis Roadmap. However, this did not result in a large research effort at the time. A major question remains how to efficiently store excess renewable electricity. One solution is to convert it into chemical energy; indeed that is the only viable solution if one is dealing with large excess of electricity. As the intelligent use of renewable energy sources is a key ambition of the Top Sector Energy, this is clearly an area with potential synergy with the Top Sector Chemistry.

To reduce the adverse effects of atmospheric CO₂ emissions on the climate, increased attention is currently being given to the **utilization of CO₂**. We distinguish three categories: (i) the reduction of CO₂ with renewable solar energy to fuels (“solar fuels”), (ii) the production of chemicals and (iii) an enhanced biological utilization. There are also

technological uses for CO₂ as such, for instance enhanced oil recovery. An important facet in the new perspective of CO₂ utilization is the conversion of excess electricity from renewable resources into preferably liquid fuels. If large amounts of CO₂ could be converted into fuels, preferably types that are compatible with our current energy infrastructure, it would mark a significant step toward cycling carbon in a way done by nature. Such approaches would reduce CO₂ emissions and also limit the extraction of fossil-carbon sources.

Challenges

The conversion of CO₂ into fuels involves its reduction, which requires energy. This energy cannot be derived from fossil resources as the amount of CO₂ produced would be higher than that of CO₂ converted into fuel. Therefore, the conversion of large amounts of CO₂ into fuels should involve renewable sources of energy such as solar energy, wind energy, hydroelectric energy or geothermal energy. If done efficiently, the **conversion of CO₂** could also be a way to solve the problem of how to **store (excess) renewable electric energy**. The most obvious choice would be to target liquid fuels such as hydrocarbons similar to current transportation fuels or methanol. Methanol would have the added benefit of also being an intermediate for the production of a wide range of chemicals. There are many ways to convert CO₂ to fuels, such as direct reduction using electric energy, photocatalytic reduction, and chemical reduction using H₂. The technologies associated with these approaches have widely different levels of technical maturity. Currently, for instance, direct photocatalytic CO₂ reduction can only be done at very low efficiency, whereas using water electrolysis to produce H₂ is proven technology, although not amenable to large-scale implementation because expensive catalyst materials are used. In virtually all of these approaches, catalysis plays an important role with significant challenges for electrocatalysis, photocatalysis, and heterogeneous and



homogeneous catalysis. On a more general level, the intermittent operation of catalytic processes under a daily cycle is becoming important, along with classic themes such as catalyst activity, selectivity and stability.

In a circular economy, CO₂ is increasingly viewed by the chemical industry as a building block, rather than a waste product. In some cases, the use of CO₂ for the production of chemicals is already at the commercial level. Efforts are underway to react CO₂ with olefins, dienes and alkynes to form carboxylates, carbonates and carbamates. Many of these processes are catalytic. Some processes are endergonic and thus more difficult to implement. Currently, many chemical processes rely on synthesis gas (CO+H₂), e.g. Fischer-Tropsch synthesis, hydroformylation and carbonylation. Opportunities should be explored to develop chemistry based on CO₂+H₂ instead of CO+H₂ as a way to functionalize hydrocarbons. However, one should keep in mind that the contribution of CO₂

conversion to chemicals towards solving the impact of climate change is limited by the order-of-magnitude smaller size of the chemicals market compared to the fuel market.

Biotechnological conversion of CO₂ involves the use of (modified) organisms to convert CO₂ into useful products under optimized conditions, e.g. the cultivation of biomass in greenhouses under increased CO₂ concentration, the growing of aquatic biomass by dissolving CO₂ in water, and the targeted synthesis of chemicals. Modifying the organisms by for instance genetic engineering is one of the possibilities to arrive at the right chemicals. An example is the Photanol concept, a Dutch SME that uses engineered cyanobacteria that directly and efficiently turn CO₂ into predetermined products when exposed to light.

Opportunities for Catalysis

The technology for solar fuels production should be robust, scalable and efficient. It should have an

operating life of longer than ten years and be based on abundant elements, and the overall system efficiency should be sufficient for it to be able to compete with non-sustainable energy generation. The intermittency of sustainable electrons will pose challenges to the future catalytic processes that store electricity. Direct electrochemical CO_2 reduction will require breakthroughs in the field of electrocatalysis and is considered a long-term target. The most likely scenario, therefore, involves water electrolysis by renewable electrons generated by photovoltaics technology or direct photocatalytic water splitting to produce the H_2 needed for the reduction of CO_2 .

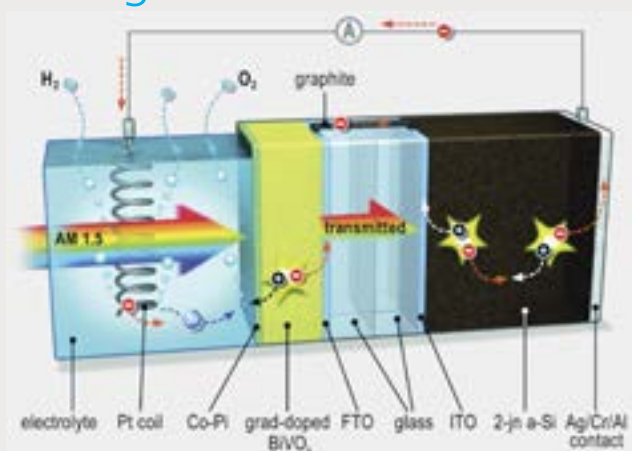
The large-scale implementation of electrolyzers for renewable H_2 production is hampered by the **low abundance of active and stable electrocatalysts** and their **inability to deal with fluctuating conditions**. Noble metals are most active for the difficult oxygen-evolution reaction. RuO_2 is the most active material, but it degrades. Usually, titania-stabilized IrO_x is used for oxygen evolution, while Pt is used for hydrogen evolution in an acidic electrolyte.

Alkaline electrolytes allow the use of more abundant materials (such as nickel, for both anode and cathode) but still suffer from an order-of-magnitude lower current. Nevertheless, alkaline electrolyzers form a very active field of research.

Integrated photocatalytic devices are increasingly being considered as an attractive alternative. There are many opportunities for improved materials for light absorption, better catalysts for water oxidation with low overpotential, the use of non-noble metal catalysts and their integration into devices in which aspects as light management also need to be considered. With regard to light absorption, the currently available semiconductors are either robust but not very efficient (e.g. TiO_2 , Fe_2O_3) or efficient but unstable (e.g. CdS , CdSe). Tandem devices are needed to reach efficiencies that can compete with PV technology. Specific challenges to catalysis are the development of better catalysts to reduce the overpotential of water splitting, especially the water oxidation reaction, and to build smart interfaces between photoabsorbing and catalytic layers.

Efficient solar water splitting

Fatwa Abdi (MECS group, Bernard Dam, TU Delft) designed a water splitting device with a 5% solar-to-hydrogen conversion efficiency using a spray deposited BiVO_4 as the photoanode. This high bandgap material captures the high energy photons and takes care of the oxidation of water. The low energy photons are converted by the Si-based PV solar cell which assures the proper potential for the water reduction at the other electrode. *Nature Communications* 4 (2013) 2195.



All of these aspects should preferably be addressed in an integrative manner. It requires input from those working at the device level, implying that design criteria for the optimal device need to be assessed a priori or along the way. It also requires close interaction between those working on the design of new semiconductor materials, (electro)catalysts, and on light and device management. Disciplines within the catalysis domain around in situ spectroscopy -to study elementary processes-, theoretical chemistry, e.g. to deal with excited states, and model studies of the cocatalyst/protective layer/semiconductor interfaces, e.g. surface science, need to be strengthened. Moreover, such an approach creates opportunities for scientists in the field of catalysis to interact with those in the fields of photo(electro)-chemistry and nanoscale preparation techniques for device development (lithography, atomic layer deposition, etc.).

If H₂ could be cheaply produced from solar energy, the **production of synthesis gas from CO₂** would be within reach. From synthesis gas, a wide range of products (methane, methanol, liquid hydrocarbon fuels) can be manufactured with established catalytic technology. Nevertheless, issues remain to be solved with respect to scaling such operations to the optimum in terms of local/centralized H₂ generation and allowing for the variable process conditions associated with the intermittent availability of H₂. Another aspect of photocatalytic reduction processes of water or carbon dioxide is that pure oxygen can be obtained as a byproduct. This byproduct stream has economic value, because the alternative route, via air separation, is very expensive.

Catalytic **CO₂ conversion to chemicals** is rapidly developing and new developments are dominated by homogeneous systems, which can selectively reduce CO₂ or build CO₂ in other molecules. The challenge here is to widen the scope of reactions and products and to develop more active and

selective catalysts. The use of heterogeneous systems for this purpose is underdeveloped, except in already existing industrial processes, such as methanol synthesis.

CO₂ is not the only option for storing excess energy in the form of chemical energy. Another opportunity is to use abundant nitrogen as the feedstock. It shares with CO₂ conversion the opportunity to use abundant stable chemicals as feedstock to fuels and chemicals.

Dutch Strengths in CO₂ Conversion and Solar Energy Storage

The strongest asset to tackle the challenge of CO₂ conversion and excess renewable energy storage is the existing Dutch network in catalysis, where academia and industry have teamed up and have an excellent track record in the successful integration of different disciplines to cope with important societal challenges. The most recent example is the establishment of a **graduate school on solar fuels catalysis** aimed at educating young scientists in this new field. Research groups from Leiden University, Utrecht University, Eindhoven University of Technology and University of Twente participate in the graduate school.

So far, the chemical industry has largely shunned significant efforts in terms of CO₂ valorization, solar fuels, etc.. However, CO₂ is increasingly being considered a building block rather than a waste product. This changing view is important to the **industry's medium- to long-term strategy**. The steel and cement industry are scouting out technologies that could reduce CO₂ emissions. Power companies are showing interest in storing excess (renewable) energy. These industrial players are often acting on the international level, if not the global level. This

means there are good opportunities for the catalysis community to increase interaction with them, capitalizing on the long standing tradition of public-private partnerships within the Dutch school of catalysis.

The CO₂ conversion topic has many dimensions. On one end of the spectrum it concerns short-term solutions to reduce the cost of electrolyzers. On the other end it involves long-term developments such as the production of chemicals and the development of integrated solar-fuel devices. Some of these aspects are best covered in public-private partnerships, in which innovation by SMEs should be strongly supported. The development of a cost-effective and scalable solar-fuels device will require a considerable long-term effort to overcome the many fundamental challenges. Among other things, considerable investments will be needed to reinforce areas of expertise such as fuel-cell catalysis, electrochemistry, inorganic chemistry, and theoretical chemistry.

Much of the expertise required to make step changes in the field of CO₂ conversion and storage

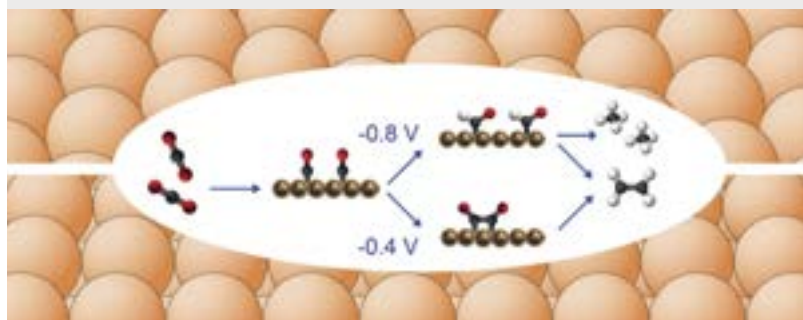
of solar energy is already present in the Netherlands. Catalysis covers a substantial part of this expertise but cannot tackle all the challenges by itself. There is a clear need to **connect the various areas of expertise**.

Research Areas & Deliverables

Areas of Research

There is a great need for a solution regarding the **storage of energy from excess renewable electricity** in chemical energy. At this point, the most viable solution seems to be to use electrolyzers since it is proven technology, although it can only be scaled up if more abundant electrode materials are developed. Renewable hydrogen can then be used to convert point-source CO₂ to fuels. Catalysts for both these processes need to be optimized to deal with contaminants present in flue gases and with the intermittency of renewable energy sources. The scale at which such operations can be done remains an important question.

Carbon-carbon bond formation on copper electrodes



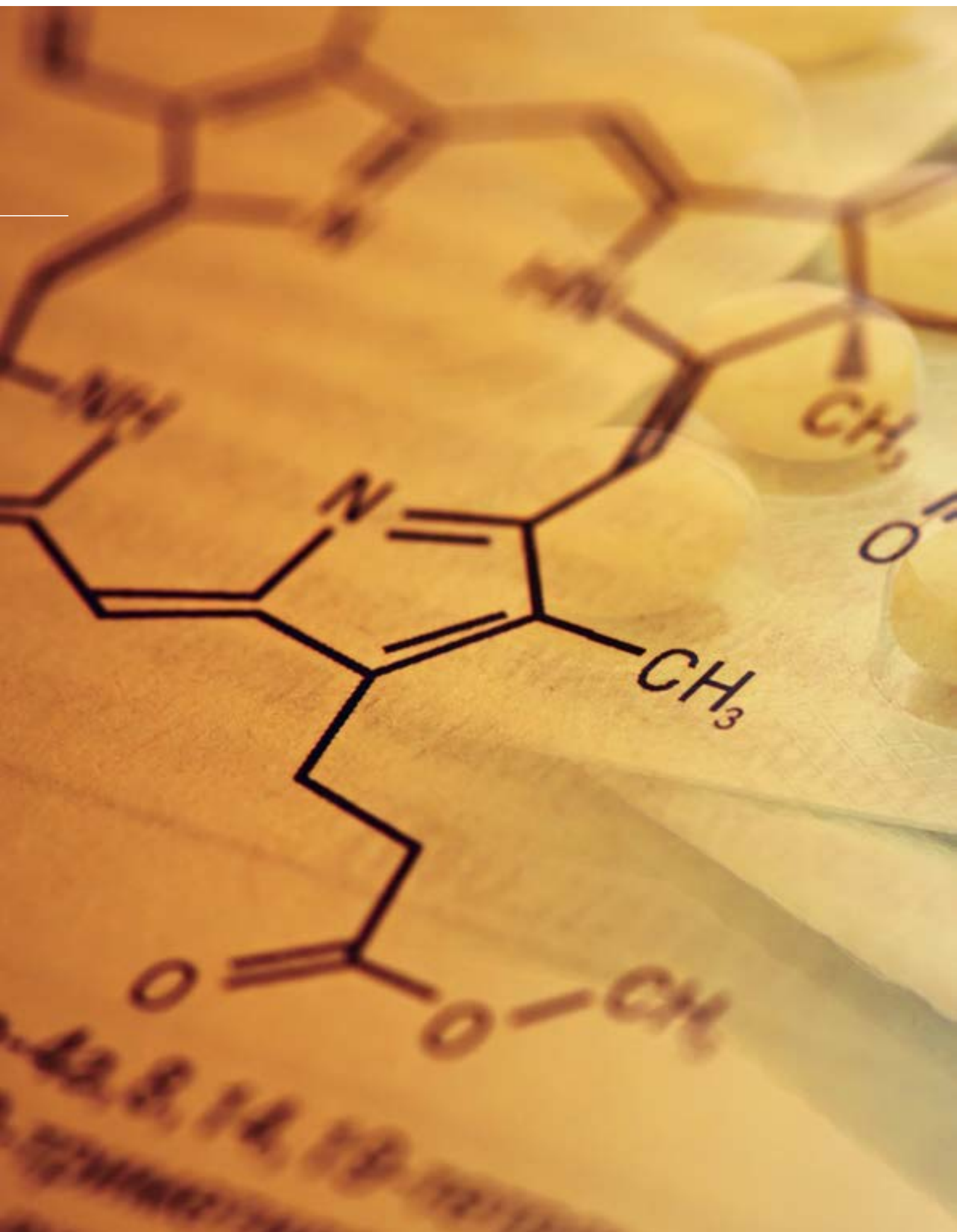
Klaas Jan Schouten from the group of Marc Koper at Leiden University (K.J.P. Schouten et al., *J. Am. Chem. Soc.* 134 (2012) 9864, *Angew. Chem. Int. Ed.* 53 (2014) 10858) discovered that the formation of ethylene from the electrocatalytic reduction of CO₂ and CO is highly sensitive to both the copper surface structure, with (100) being most suitable surface, and to the solution pH, with alkaline electrolyte being the preferred medium for efficient C-C bond coupling from CO. These findings have significant implications for the design of better electrocatalysts for selective CO₂ reduction.

The development of **integrated photocatalytic/photoelectrochemical devices** to produce H₂ is another important area of research for the coming decades. The challenge is to develop both cheap materials for photo absorption and new catalysts and then to integrate those in a device with an overall solar-to-hydrogen efficiency of at least 20% in order to compete with photovoltaic/electrolyzer technology. This will require improved characterization methods for studying photochemical processes in relation to photocatalysis as well as new computational chemistry to deal with specific issues of photocatalyst systems. Another type of integrated device would have to be developed for storage of renewable energy in the form of chemical energy. The development of integrated devices will require a systems-catalysis approach that includes such engineering aspects as small-scale and intermittent operation.

In the long term, the focus will be on **highly integrated solutions enabling the carbon-neutral production of energy** in all areas, including mobility and chemicals. To arrive at this desired situation, technology capable of capturing CO₂ from the atmosphere will need to be developed. This may involve artificial leaf approaches, in which CO₂ from the air is photocatalytically converted into useful products or intermediates, or approaches in which CO₂ capture is followed by conversion, either electrochemically or by renewable H₂. Biomimetics as well as genetically modified organisms may also be an option. In such a scenario, where humanity no longer depends on fossil resources for energy, these resources (including biomass) could become the starting chemicals for the production of consumer products. CO₂ would no longer be a waste product but would be considered a primary building block. New catalytic processes have to be developed that will allow for an efficient use of CO₂ as a monomeric unit in the production of fuels and chemicals.

Deliverables in 10-20 years

- Scalable electrolyzer technology based on cheap and abundant catalytic metals to convert renewable electricity into hydrogen;
- A device with a solar-to-hydrogen generation efficiency $\approx 20\%$, beating the efficiency of PV technology;
- Catalytic technologies to store renewable electricity and/or renewable hydrogen in liquid fuels;
- The integration of solar energy and CO₂ use in chemicals and fuels production.



Catalytic Synthesis of Bioactive Molecules

6

37

As the world has a continual need for a variety of new bioactive compounds with possible applications in the food, feed, and health industries, it is of key importance to be able to develop new catalytic tools to make the organic synthesis of bioactive molecules more efficient. These tools will reduce the related costs and make synthetic routes more sustainable. This means that new and improved, environmentally benign catalysts need to be developed, taking full advantage of the exciting new tools and methods being developed in both biocatalysis and chemocatalysis. These new systems will enable cost-efficient one-pot cascade reactions and are expected to give access to a variety of new, selective synthetic reaction types, allowing the efficient synthesis of a wide variety of bioactive molecules.

Status & Challenges

Current Situation

As a key enabling science, synthetic chemistry allows the preparation of a wide range of (complex) bioactive molecules. This includes all the vital molecules that change our daily lives, e.g. medicines, antibiotics, hormones, vitamins and fungicides, or influence them indirectly, e.g. insecticides, food additives, fertilizers, and toxins. It also includes those molecules that make our lives more agreeable, e.g. personal-care ingredients, fragrances and flavors. All these molecules are of high relevance for the pharma, agro and health & food sectors. Therefore this is the field where the Top Sector Chemistry has an excellent opportunity to join forces with the Top Sectors Life Science & Health and AgriFood.

Organic chemistry has matured to such an advanced level that almost any desired molecule can be synthesized. At the same time, however, the synthetic chemistry of most bioactive molecules is dominated by stoichiometric chemistry, the abundant use of protection groups, and many consecutive reaction steps generally requiring elaborate work-up procedures after each reaction step. This typically leads to high costs, waste formation and unnecessary energy consumption. Several examples have illustrated the huge potential of catalysis in organic synthesis, providing efficient short-cuts in the overall route. The various cross-coupling reactions (2010 Nobel Prize) and olefin metathesis reactions (2005 Nobel Prize) used abundantly in organic synthesis are especially noteworthy. The field has made considerable progress since the last Roadmap for Catalysis, and numerous catalytic processes have been implemented, including C-C bond reactions, hydrogenations, catalytic oxidations, and carbonylations. Nevertheless, there remains much room for improvement. Plenty of stoichiometric

steps still need to be replaced by catalytic processes, for example. Catalysis still offers many opportunities for synthetic shortcuts.

Elegant and useful chemo-, regio-, diastereo- and enantioselective catalytic reactions have been introduced to the field as well, using both synthetic homogeneous catalysts (2001 Nobel Prize) and enzymes. This clearly has boosted the efficiency of preparing enantiopure compounds and has led to substantially improved selectivities. However, the development of enantioselective catalysis, among other selective types, has by no means matured to the desired level. Many of the known reactions have a limited substrate scope or require the development of a dedicated catalyst or enzyme. Similarly, the development of one-pot cascade-type catalytic reactions, using either one catalyst mediating several subsequent coupled reaction steps or a mix of multiple catalysts performing different tasks, is slowly setting the stage. Yet, like enantioselective catalysis, the development of catalytic one-pot reactions is still in its infancy.

Challenges

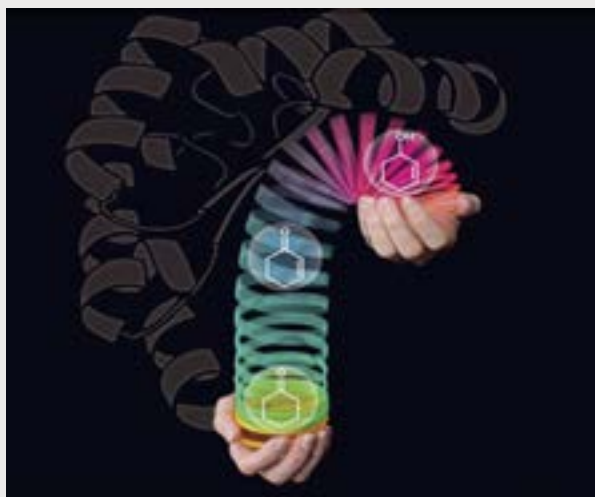
The world has a continual need for a variety of new bioactive compounds. Several food-, modern-lifestyle- and aging-related health issues make it important to develop new or improved drugs, food ingredients and personal-care-product ingredients. Cities with large populations are in serious danger of developing untreatable diseases because bacteria are becoming increasingly resistant to the antibiotics currently available. Furthermore, to produce enough food for our rapidly growing world population it is of crucial importance to be able to grow crops in the most efficient manner possible. This, in turn, requires the development of new, safe and bioselective antibiotics, insecticides and fungicides that are harmless to other organisms such as honeybees, mammals, and birds.

If we are to meet the challenges presented above, the **integration of knowledge and expertise** in organic synthesis, homogeneous catalysis and biocatalysis **is crucial**. This needs to be combined with efficient reactors, microflow devices and continuous-reaction modes rather than with the batch reactions common in fine chemistry. Furthermore, the field of bioactive molecules is highly dynamic. Compounds considered relevant today may well be outdated next year. Hence the field needs to be constantly updated with knowledge from hospitals, pharmacy and the agrochemical and food sector including all stakeholders. Furthermore, as the diversity of compounds relevant to the medicinal, agrochemical, food and personal-care industries is very broad, it is more appropriate to define targets in terms of new (selective) catalytic tools for the synthesis of bioactive organic molecules rather than to target a specific molecule. These new tools should be as cheap, as fast and as selective as possible, and they should have a broad substrate scope.

Opportunities for Catalysis

There are very many opportunities for catalysis when it comes to contributing to the efficient synthesis of bioactive compounds. Below, we group them in two categories: opportunities whereby catalysis is an enabling tool in synthesis and opportunities whereby catalysis can make synthesis more environmentally friendly and cost efficient.

Catalysis will enable **synthesis routes with fewer** (but preferably no) **protection groups** and disclose new transformations towards the desired products that provide synthetic shortcuts, for example through the activation of bonds. Catalytic synthesis is expected to create new reactions for making cyclic compounds, both heterocyclic and purely carbocyclic. In biocatalysis, combining bioinformatics (analysis of the metagenome) with enzyme development should lead to the discovery and development of new enzyme activities. Using non-toxic first-row transition metals as catalysts or metal-free catalysis will contribute to reducing chemistry's dependence on scarce elements. Finally,



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Multi-Enzymatic cascade reactions

Multi-Enzymatic cascade for the redox neutral isomerisation of allyl alcohols to ketones. By combining several enzymes it became possible to reduce one group within one molecule while oxidising another. Normally oxidising reagents and then reducing reagents need to be added to achieve this, here it is possible without any of these reagents, significantly lowering the environmental burden of the reaction - and its cost.

catalysis will lead to higher chemo-, regio-, diastereo- and enantioselectivity in chemical transformations, preferably with a broad substrate scope.

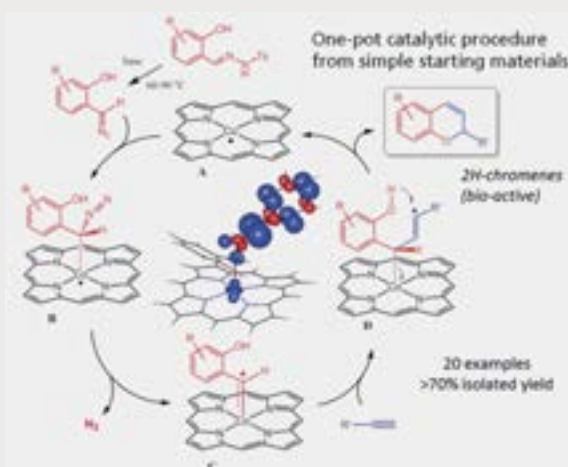
Another important target is the transformation of stoichiometric reactions into catalytic ones. Mechanistic research will enable the development of active and robust catalysts with high turnover frequencies (TOF) and turnover numbers (TON), leading to economically viable processes. Improving on the current situation for one-pot cascade processes is expected to yield **more efficient synthesis requiring less high-energy reagents**. Lastly, using immobilized catalysts and enzymes will enable the development of continuous reactions rather than batch reactions.

Catalytic methods in complex organic synthesis involve either homogeneous or biocatalysis. The combined use of (chemo and/or bio) catalysts allows **one-pot cascade-type reactions preventing elaborate (waste-generating) work-up procedures** and/or the strict need to protect groups. Important

goals in this field are to develop smart, efficient, short-cut synthetic routes, using cheap and non-toxic catalysts based on first-row transition metals (or even metal-free) catalysts and to develop innovative ways to make such catalysts and biocatalysts mutually compatible. Interesting new methods to steer us towards these goals include the following: smart ligand design; screening for new enzymes in the metagenome; making many variants of one type of enzyme available; modifying enzymes through site-selective mutagenesis through directed evolution or rational design or a combination thereof, i.e. smart libraries and synthetic biology (modifying natural enzymes with chemical components); compartmentalization; open-shell (radical-type) organometallic catalysis; and supramolecular approaches in catalysis. All of this should contribute to more efficient synthetic routes that will generate less waste, be less time consuming and generally lead to a cheaper and easier production of bioactive compounds.

A Metalloradical Approach to 2H-Chromenes

The group of Bas de Bruin (University of Amsterdam) developed a new efficient one-pot cobalt-catalyzed procedure for the synthesis of 2H-chromenes (N. D. Paul, et al., J. Am. Chem. Soc. 136 (2014), 1090–1096). These are important structural motifs that exist in numerous natural products and medicines, possessing interesting biological activities.



Dutch Strengths in Catalytic Synthesis of Bioactive Molecules

The Netherlands has traditionally had strong academic research groups in synthetic (enantioselective) chemistry and catalysis, with a current emphasis on catalysis, for example at the University of Amsterdam, University of Groningen and Radboud University Nijmegen. The relatively few but nevertheless excellent groups in homogeneous catalysis and biocatalysis (involved in the development of new catalysis tools) as well as in organic synthesis (who apply those tools) form a strong basis for a powerful development in the area of clean and efficient organic chemistry based on catalysis. This basis is further strengthened by the computational groups that are in part incorporated in, or linked to, the groups that are developing catalysts, both in the area of homogeneous catalysis and biocatalysis. The connections with the agro and food sectors form another strong point in the Netherlands, as those give unusual and fruitful input to the catalysis community. Likewise, linking-up with companies that are entering the market from a renewable building-block perspective offers another opportunity in the field of catalysis for bioactive compounds. This includes vanillin and xylitol from wood (lignin) as well as cholesterol lowering ingredients. The catalytic technology needed to convert renewable building blocks into useful chemicals overlaps with the catalysis needed for bioactive molecules. For example, catalytic ester hydrogenation can be used to reduce highly oxygenated building blocks, but it is also useful to replace the stoichiometric (and hence expensive) hydride-reduction technologies currently used in the fine-chemical sector. Synthesis as an enabling science for many areas of research is well connected to catalysis and there is a strong collaborative

network that facilitates new initiatives being taken up and made successful.

The pharmaceutical sector has traditionally been a natural industrial partner of all synthetic groups. With the gradual disappearance of the larger pharmaceutical companies from the Netherlands, new opportunities to take over arise for smaller, more specialized companies such as Synthon, Mercachem or Syncom as well as for new start-ups. The emergence of these new players in the pharmaceutical sector and the companies in the agro and food sectors that are new to the catalytic community might induce changes in the current way of collaborating in the current PPP-initiatives. Both industry and universities are likely to profit from creating a new joint field of overlap.

Research Areas & Deliverables

Areas of Research

A key problem in the chemical synthesis of bioactive compounds is inefficiency. The main product obtained is often waste, rather than the desired compound. Both atom and energy efficiency are important when it comes to reducing industrial production costs and moderating our ecological footprint in a circular economy. To solve these issues, three strategies have been envisioned.

To enable cost reductions, it is of crucial importance to develop improved, environmentally benign catalysts based on abundant metals or enzymes. They should be cheap and safe, allow for catalyst recycling and lead to high TONs and TOFs. Furthermore, they should also enable new selective catalytic synthetic reactions that do not rely on protection-group chemistry. In chemocatalysis the development of environmentally benign catalysts will be made possible by utilizing a variety of bio-

inspired tools based on both “cooperative” and “redox-active” ligands. A transition from the use of rare and noble metals to abundant and cheap, first-row transition metal catalysts is typically associated with a switch to entirely different (radical-type) reaction mechanisms. Selective radical-type processes are certainly possible in the coordination sphere of transition metals, as a variety of highly selective enzymatic radical-type processes have demonstrated. Equally selective radical-type processes will be developed with synthetic chemocatalysts. Mechanistic research is crucial if we are to arrive at the desired catalyst improvements and cost reductions. Understanding the behavior and reactivity of metallo-radicals and metal-bound “substrate radicals” during catalytic turnover is crucial. This applies both to the development of catalysis with abundant metals and to uncover new, selective (one-pot, cascade-type) radical-type reactions such as C-H bond functionalization and catalytic radical-type ring-closure reactions without the need for using protection-group strategies. Besides catalyst activation, also catalyst deactivation pathways should be studied, as deactivation is frequently an important reason for low total TONs and decreasing TOFs over time. Biocatalysis is of course the obvious alternative approach if we are to develop environmentally benign catalysts. In biocatalysis, major steps forward will be made, extending the currently limited spectrum of enzymes by tapping into the vast number of the biosynthetic enzymes that nature utilizes for the synthesis of very complex structures. By way of metagenomics and sequencing, this toolbox is now coming into reach. Progress towards this goal further assisted by the fast robotic synthesis of DNA, making all enzymes essentially commercially available, scalable and thus affordable.

Cost-efficient one-pot cascade-type reactions will be developed based on sustainable starting materials replacing step-by-step syntheses with many

purification sequences. To enable this, catalyst immobilization, compartmentalization of catalysts (e.g. in MOFs or supramolecular capsules) and flow systems for cascades will be studied.

The results will be drastically shortened synthesis routes. When several enzymes that do not belong to one natural route are combined and co-expressed in one organism, the cascade can be realized immobilized inside cells. Combining enzyme catalysis with chemocatalysis offers further exciting prospects. This also holds for the combination of chemo- and biocatalysis with fermentation. In particular, the synthesis of non-natural antibiotics in combined approaches is very valuable and to some extent already a reality.

The abovementioned new and improved catalysts should enable a variety of new, selective synthetic reaction types that are catalytic and do not require protection-group chemistry. Challenging new C-C bond formation strategies, (radical-type) ring-closing reactions and C-H bond functionalization strategies will be developed. Additionally, the replacement of C=O by carbene precursors, isonitriles and other building blocks will be investigated, aiming for the development of new, generally applicable synthetic methodologies. The currently very polluting amide synthesis as well as heterocyclic chemistry will be converted into catalytic chemistry based on biocatalysts and homogeneous catalysts. In particular, nitrogen containing heterocycles and complex (hetero)cyclic compounds demand new catalytic approaches that can be of an equally revolutionary power as cross-coupling reactions. New homogeneous catalysts will be developed and biocatalysis will be expanded from degrading enzymes to synthetic enzymes. This approach has been developed in part for peptide synthesis, but the scope needs to be broadened to a variety of other amides.

Deliverables in 10-20 years

Development of improved or environmentally benign catalysts

- Catalysts based on readily available metals and ligands;
- Mutually compatible chemo- and biocatalysts;
- Mechanistic insights that enable the desired catalyst improvements (cheap and safe metals, catalyst recycling and increasing TONs and TOFs) and, hence, cost reductions;
- Reduction, recycling and replacement of key building blocks for catalysis (e.g. P-ligands);
- Biocatalysis readily available as a standard tool.

Cost-efficient one-pot, cascade-type reactions

- Efficient synthetic catalytic shortcuts;
- Of-the-shelf ordering of tailor-made and designed enzymes;
- Application of new catalytic methods in commercial processes;
- Better catalyst recovery methods (Late transition metal catalyst);
- Continuous reactions for enzymes and homogeneous catalysts.

New, selective synthetic reaction types

- Transition from stoichiometric chemistry to catalytic chemistry;
- New methods to run cascades from low-energy starting materials;
- New catalytic processes with new (bio)catalysts running with low catalyst loading and achieving high TOF and TON values;
- New reactions towards polycyclic and heterocyclic compounds;
- Development of entirely new catalytic reactions to facilitate (chemo-, regio-, diastereo- and enantioselective) organic synthesis.



Precision Synthesis of Functional Materials

45

A major inroad into innovation for polymeric materials will be the design and catalytic synthesis of functional polymeric materials displaying targeted properties. This involves both the bulk as well as the surface of the material. Precision catalysis with novel methodologies can play an important role in polymerization, cross-linking, degradation and (post-polymerization) surface modification. It is applied to influence the chemical nature of the material as well as the temporal and topological aspects of its function. The increased introduction of catalytic concepts within materials-surface science may lead to important breakthroughs in the manufacturing of functional polymeric and hybrid materials.

Status & Challenges

Current Situation

In synthesizing functional materials, one aims to control the properties and functionality of the bulk material or its surface. This includes controlling its identity (chemical nature), as well as certain temporal (order of events) and topological aspects (position, micro-meso-macro length scales). Catalysis plays an important role in polymerization, cross-linking, degradation, and (post-polymerization) surface modification. As such, tailor-made (high) performance polymers and composites were included in the previous Catalysis Roadmap as a goal. However, this did not result in a large research effort at the time. Novel catalytic methods might improve material performance, but they could also help to improve processability or to lower the ecological footprint in various ways. In this way, catalysis also contributes to meet increasingly strict Health, Safety, Environment (HSE) regulatory constraints. Examples include more sustainable and safer production methods, lower production cost, lower energy consumption in the production process or by the customer, and control over service life-time, recyclability and degradation. These are all –technological- aspects of a circular economy. The production of such smart materials is one of the ambitions of the Top Sector Chemistry. There is ample opportunity for integration with the Top Sector High Tech Systems and Materials (HTSM), as the application of these smart materials is key in this Top Sector.

A limited number of polymerization technologies currently prevail, viz. Ziegler-Natta catalysis for polyolefins and polycondensation for engineering plastics and coatings (polyesters, polyamides, polysiloxanes). Other technologies comprise (controlled) radical polymerizations (in particular Reversible Addition-Fragmentation chain Transfer or RAFT) and cobalt-catalyzed oxidative curing, but

also other types of curing catalysis like the vulcanization of rubber or curing catalysis as a tool to enable the self-healing of materials. Novel catalytic polymerization tools are being added to the toolbox, e.g. metathesis, “C₁” (carbene) polymerization, copolymerization of alkenes with other monomers such as CO, carbene precursors, epoxides, aziridines, cyclopropanes, cyclopropenes, alkynes, polar vinyl monomers and enzymatic polymerization.

Challenges

Despite its huge industrial importance, polyolefin (PO) catalysis mostly uses a heterogeneous Ziegler-Natta catalyst that is still poorly understood. Increasing our level of understanding of this type of heterogeneous catalysts is highly desirable as that would allow better fine-tuning and control of the polymer properties. In general, the challenge in catalytic technologies for PO synthesis is the control of the product microstructure by a suitable catalyst. This includes the use of block copolymerization, the control of bimodality, and the inclusion of a polar functionality in the product material, which for example could render the material oil-resistant or lead to improved adhesion. To that end, polymerization catalysts are needed, including those that allow block copolymerization and those that accept monomers functionalized with heteroatoms. Such monomers may go beyond olefinic monomers. From a long-term perspective, the shale gas revolution challenges the economic viability of traditional PO feedstocks and may prompt us to consider methane as an earth-abundant hydrocarbon not currently considered as a monomer to access polyolefins. With vinyl monomers instead of simple olefin monomers, the aforementioned needs can be (partly) met by controlled radical polymerization, which, as exemplified by RAFT, is characterized by a broad functional group tolerance. Still, this RAFT approach faces challenges related to the cost and large-scale availability of the required control

agents, color and/or malodor generated by sulfurous RAFT agents, color and/or toxicity as well as to the lack of functional group tolerance of transition metal-based agents.

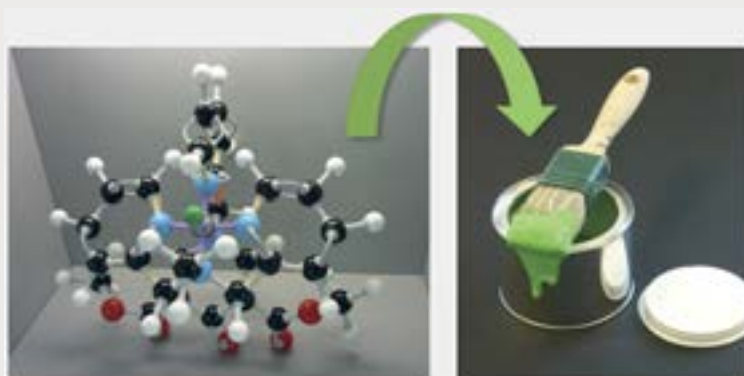
Polycondensation catalysis for polyesters, polyamides, and polysiloxanes is still a largely unexplored territory for the catalysis community. The catalytic reactions form a complex kinetic network with poorly understood multiple equilibria. So far, we have little control over undesired transesterification or amidation, we have little control over molecular weight/distribution, and we have little control over chemoselectivity (e.g. the distinction between aryl and alkyl monomers). There is also a need for methods that will allow selective end-group functionalization without breaking the polymer chain. Gaining control of these aspects would mean getting closer to true precision synthesis. Another challenge concerns the

development of lower-temperature technology, which is desirable for reasons of life-cycle-assessment (LCA) impact, atom efficiency, selectivity control, and the extra opportunities for the use of thermolabile monomers. HSE regulation might prompt us to look for low-toxicity substitutes for the current tin catalysts, as well as for catalytic technologies to recycle these materials. The development of “restriction catalysts” that would cut the bond between specific monomers analogous to enzymatic degradation is an interesting option here.

There are also various challenges arising from (autooxidative) **curing and vulcanization** as application areas. Here, too, HSE regulations put pressure on the development of substitutes for the widely applied cobalt catalysts for autooxidative curing of alkyd resins. The development of efficient reversible rubber-vulcanization technologies

The quest for cobalt-free alkyd paint driers: iron and manganese based alkyd paint drying catalysts

Hage, Gibbs and co-workers published an overview of paint drying catalysts (J.W. de Boer, et al, Eur. J. Inorg. Chem., 2013, 3581). Alkyd-based paints need catalysts for oxidative curing. Due to a probable classification of the widely used cobalt carboxylates, the coatings industry is seeking alternative oxidative drying catalysts. Various manganese and iron paint driers containing polydentate ligands show good paint drying activity. The most active manganese and iron catalysts were previously identified as stain bleaching catalysts in detergents, and are effective for alkyd paint curing via similar mechanisms as those exhibited for oily food stain bleaching.



presents another challenge that addresses the increasing need for efficient recycling technologies. Catalysis is generally expected to contribute to the development of polymers that can reversibly be depolymerized and triggered (bio)degradation, addressing environmental problems (e.g. “plastic soup”). Another challenging area concerns the research and development of latent catalysts that become active in curing or self-healing on demand and can be included within the product.

Finally, there are also various challenges arising from the limitations of the technologies that are currently employed in the **post-polymerization surface modification** of materials. The most widely used method, i.e. plasma treatment, requires specialized, dedicated equipment, is very aggressive and unselective, and suffers from a lack of topological control. A key requirement is that the bulk properties of the polymeric material not be significantly altered, e.g. by undesired chain-breaking reactions. Evidently, especially the surface modification of polyolefins presents a very challenging task, given the very unreactive nature of the aliphatic methylene groups.

Opportunities for Catalysis

An attractive opportunity would entail **integrating the current catalytic approaches** to the precision synthesis of functional materials **with process intensification, biocatalysis, and traditional polymer science**. A number of ongoing projects in the Dutch Polymer Institute (DPI) deal with polymerization catalysis or offer opportunities for including this. More specifically, this integration includes catalysis for polyolefins, performance polymers, functional polymers (e.g. responsive materials), and coatings of various sorts (e.g. daylight photo-initiated curing systems or drug-releasing biomedical coatings).

The **use of renewable feedstocks** should be incorporated here. Catalysis not only plays a crucial

role in the generation and further conversion of monomers from carbohydrates as feedstock, but also in the valorization of other plant-derived feedstock streams. Successful valorization of all streams is a prerequisite for success in biomaterials. In this respect, the most recalcitrant streams at the moment are lignin and humins, see also the challenges presented in Chapter 4. These streams are expected to serve as feedstock for biobased thermoset resins, e.g. as substitutes for phenol/formaldehyde resins.

Biocatalysis for material-science applications is an active and fast-growing field of research. Significant progress has been achieved in this area, not only with respect to enzymatic polymerization catalysis, but also with respect to enzymatic surface modification. New biocatalytic polycondensation technologies appear particularly well suited to deal with thermolabile monomers. Current commercially applied polymerization technologies are dominated by chemocatalysis.

For catalytic surface modification, research on chemocatalytic approaches strongly lags behind enzyme catalysis. There are clear **opportunities for both bio- and chemocatalysis** in this area, **with strong synergism arising from exchanging reactivity concepts**. Recent approaches in homogenous catalysis such as ligand-assisted catalysis or outer-sphere catalysis should be explored as leads for new concepts in catalyst design. This approach of learning from other disciplines can be extended to include biocatalytic enzyme design rules with respect to primary, secondary, tertiary, and/or quaternary structure. This way of thinking may lead to solutions for longstanding problems in polycondensation technology such as chemoselectivity control by monomer distinction and selective end-group functionalization without chain breaking. Clear opportunities also arise from the need to achieve improved control of material properties by a better understanding of the various

types of commercially relevant heterogeneous polymerization catalysts, such as Ziegler-Natta and siloxane polycondensation catalysts. An interesting approach with many opportunities towards improved materials is the development of hybrid materials made of polyolefins and engineering plastics. To achieve formation of such hybrid polymers, the integration of multiple catalytic cycles is required. The development of a heterogeneous block-copolymerization catalyst is also of great interest in order to achieve better control of material properties. Block copolymerization in general offers many opportunities to improve the current situation. Organocatalytic approaches appear to be of particular interest, given the increasing pressure imposed by HSE regulations to avoid toxic metals. Single-Electron Transfer Living Radical Polymerization (SET-LRP) is one of the more interesting new developments with potential to meet industrial demands given the sub-ppm level catalyst loadings.

The development of efficient polycondensation or curing **catalysts based on non-toxic, earth-abundant metals** as substitutes for the above-mentioned tin and cobalt catalysts presents another opportunity for chemocatalysis. Obviously, bio- or organocatalysis may also offer solutions that are acceptable from an HSE point of view. The **transition towards biobased monomer production** (e.g. from fermentation) offers an opportunity to rethink the traditional process routes. If, as in the case of polycondensates, monomers need to be activated before polymerization, they could be activated directly through an appropriate catalytic process. This would require the integration of multiple catalytic cycles, see also the research areas paragraph in Chapter 8 Integrated Multi-Catalyst Multi-Reactor Systems. Integration of bio- and chemocatalytic cycles may require development of enzymes that operate efficiently in media that allow sufficient solubility of the polymeric material.

Taking it yet another step further would mean considering the design of new polymer systems as well.

Dutch Strengths in Precision Synthesis of Functional Materials

Research and production of functional materials will remain present in developed countries such as the Netherlands despite the trend of shifting the production of polyolefins to countries with low energy prices and easy access to raw materials. There is no trend of relocating the production of coatings and paints to low-cost countries, since these are always produced locally for economic reasons.

Academic studies on PO catalysis focus mainly on well-defined single-site metallocene homogeneous catalysts, rather than on the multiple-site heterogeneous Ziegler-Natta catalysts that are used in industry. In the Netherlands, a number of well-respected academic groups in this latter area have been discontinued. Many of the catalysis-related problems within polycondensation of polyesters, polyamides, and polysiloxanes have not traditionally been part of the research areas addressed by the Dutch catalysis community. As a result, **crucial expertise** in and knowledge of both PO and polycondensation catalysis **is currently primarily present in Dutch industrial laboratories**. For polyolefins these are for example Dow, Sabic, Lanxess, and DSM, and for polycondensation AkzoNobel, DSM, and Avantium should be mentioned. However, there is sufficient knowledge of and expertise in homogeneous catalysis, heterogeneous catalysis and biocatalysis available in the Dutch academia to meet industrial challenges. Establishing novel collaborations

between these two communities is the key to success in this regard, e.g. via matchmaking activities leading to joint research projects. Research on materials from renewable feedstocks clearly demonstrates that this approach is successful and is leading to research areas of joint interest to both academia and industry, as exemplified by various existing (e.g. CatchBio) and new (e.g. InSciTe) PPPs. The **growing importance and strength of the biobased materials area** within the Netherlands is illustrated by various Dutch companies active in the field, such as Avantium (FDCA), DSM (succinic acid), BiChem (isosorbide), and Corbion (lactic acid). Catalysis research for functional materials may also benefit from Dutch academic and industrial expertise on radical polymerization and supramolecular chemistry, not only in terms of designing new materials with improved properties, but also in terms of designing new catalysts to address challenges such as chemoselective polycondensation or end-group modification.

Research Areas & Deliverables

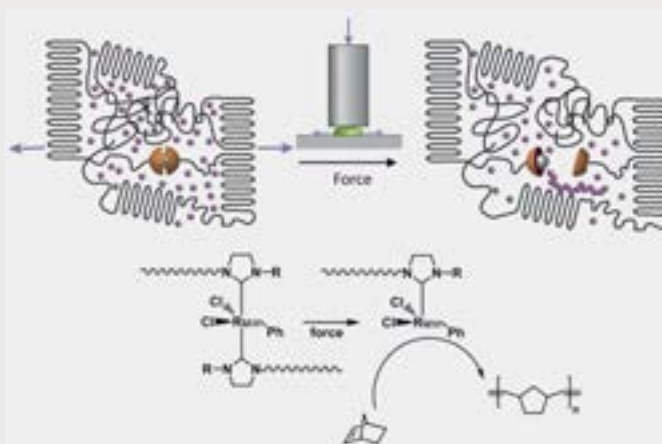
Areas of Research

The challenges stated in the foregoing sections call for the following two research approaches. Firstly, we should aim for a **better understanding and better control of the properties of polymers** resulting from either PO or polycondensation catalysis. Examples of what this understanding and control would lead to are a better defined molecular weight (distribution), chemoselective polymerizations, selective end-group functionalization, the incorporation of polar monomers and block copolymerization. Most likely research into new or modified catalysts for these reactions will be included. A specific area of catalyst development is formed by the latent, “on-demand” polymerization catalysts for curing or self-healing. Finally, we highlight post-polymerization surface modification through bio- or chemocatalysis here as a less conventional way to engineer polymer properties.

Mechanically induced activation of a polymerization reaction

Rob Jacobs and Rint Sijbesma (TUE) developed latent metathesis catalyst with polymer chains attached to the ligands (R. T. M. Jakobs et al., ACS Macro Lett., 2013, 613–616). Mechanical deformation of a polymeric material removes one of the ligands from the ruthenium center and thus activates the embedded catalyst for the ring opening polymerization of norbornene. The responsive material demonstrates a promising new approach to self-healing materials.

Reprinted (adapted) with permission from R.T.M. Jacobs et al., ACS Macro Lett. 2013, 613–616. Copyright 2013, American Chemical Society.



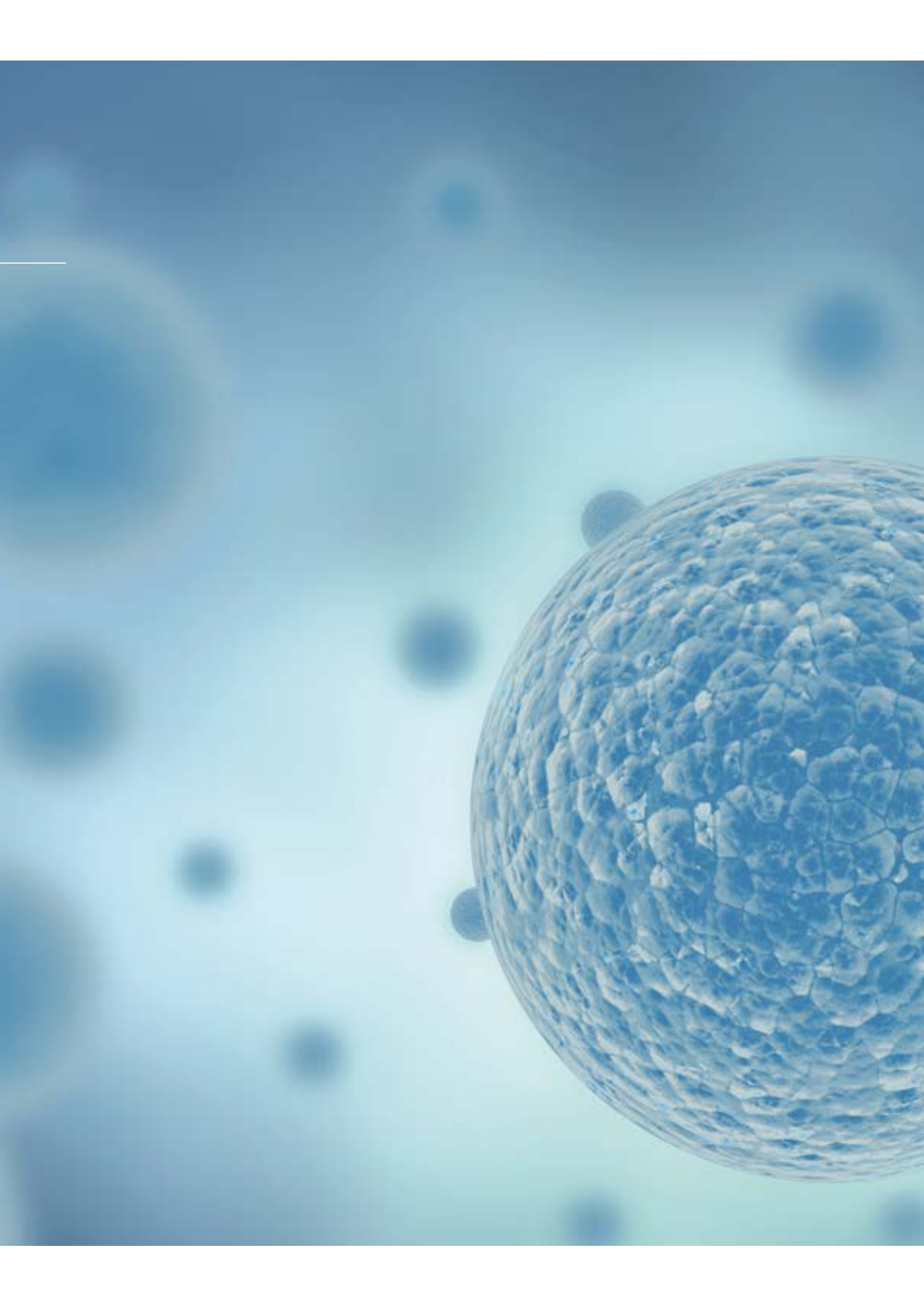
Secondly, **alternative polymerization technologies** should be explored. These would include controlled radical polymerization technologies (e.g. RAFT and SET-LRP) with low-cost, universal applicability and excellent functional group tolerance without toxicity, odor and/or color issues. Also new (advanced) polymerization technologies based on new monomers, including non-olefinic monomers such as carbene precursors, epoxides and aziridines, as well as methane as an earth-abundant, non-traditional monomer, should be mentioned here. A particular alternative technology is formed by the integration of multiple catalytic cycles that enable formation of hybrid materials made of polyolefins and engineering plastics.

In both of these research areas, we have to keep in mind the increasingly **strict LCA and HSE requirements**. These requirements do not lead to a distinctive research area in itself but may be a driver towards low-temperature PO or polycondensation technologies. Also more attention for the recyclability of polymers (e.g. via reversible rubber-vulcanization technologies), materials and polymerization technologies based on renewable monomers, and catalysts based on earth-abundant, non-toxic metals, biocatalysts, or organocatalysts.

Deliverables in 10-20 years

The ultimate goal in polymerization catalysis is to allow any set of monomers to be polymerized in a controlled manner in any desired order to achieve the desired properties of the material while meeting all application, HSE, and LCA requirements. Deliverables that are more realistic given the time-span of 10-20 years are outlined below. In all cases, “industrial applicability” is an important component of the deliverables that is not specified separately.

- A tunable, heterogeneous polymerization or block co-polymerization catalyst for both simple and polar olefins;
- An integrated catalytic system based on multiple cycles for the formation of hybrid materials made of polyolefins and engineering plastics;
- Polycondensation catalysts that meet HSE requirements and are selective with respect to the control of molecular weight (distribution) and distinct monomer reactivity;
- Curing catalysts that meet HSE requirements;
- Catalytic technology for post-polymerization control of material properties: selective end-group functionalization without chain breaking, surface modification of polymers as a substitute for plasma treatment;
- Controlled (radical) polymerization technologies for polymerization and block co-polymerization, also of highly functionalized monomers;
- Low-carbon-footprint technologies: low-temperature polycondensations, recycling via easily depolymerizable polymers (e.g. via reversible rubber vulcanization), materials based on renewable monomers;
- Latent, “on-demand” polymerization catalysts for curing or self-healing;
- Polymerization technologies for (advanced) new and drop-in materials based on non-conventional monomers, e.g. epoxides, aziridines, but also methane as earth-abundant, non-traditional monomer.



Integrated Multi-Catalyst Multi-Reactor Systems



53

Biology provides compelling demonstrations of what may be achieved by the integration of many different catalysts into a single system. The development of synthetic multi-catalyst (multi-reactor) systems has been identified as one new strategic direction in which the Netherlands has a combination of strengths that is unique in the world. Two complementary approaches have been identified: The first aims at improving the efficiency with which chemicals are produced by integrating modular catalytic systems in a plug-and-play fashion within a flow system (also known as the “LEGO” approach). The second approach aims at the integration of multiple catalysts in a single environment in which catalytic processes influence each other through multiple feedback loops, with the ultimate aim of synthesizing life de-novo and producing a synthetic cell. Both approaches touch on the concept of molecular complexity, in which control over different length scales and timescales is crucial.

Status & Challenges

Current Situation

Integrating multiple catalytic reactions into a single system is an important challenge across the fields of homogeneous catalysis and biocatalysis. Integration can improve the efficiency of catalytic processes as well as lead to entirely new functions. Biology provides many compelling examples of sophisticated functions that emerge as the result of combining different catalytic processes. The fields of synthetic biology and biotechnology utilize a top-down approach, modifying existing biological systems to engineer new functions. These can range from the production of a specific chemical to systems capable of computing based on chemical inputs. The bottom-up approach to complex catalytic systems is currently underdeveloped and constitutes an important direction for future research. Man-made catalytic systems are free from the restrictions inherent to biology, permitting the use of a wider range of experimental conditions and allowing the targeting of a wider range of functions. At the same time, engineering complex catalytic systems will deliver new fundamental insights and is likely to lead to the discovery of new and inherently unpredictable emergent functions.

The majority of synthetic catalytic systems in homogeneous catalysis and biocatalysis operate with only one reaction, only one catalyst and only one reactor. There is a recent trend towards combining multiple catalysts within a single system or device: the so-called **catalytic cascade or domino reaction**. In the bulk (petro)chemical industry the aspect of process intensification by combining multiple catalytic functions is already much further advanced and several processes operate based on multiple catalysts arranged in a stacked bed. Another important example of a multi-catalyst device in heterogeneous catalysis is the use of spatially and temporally separated reduction

catalysts and NO_x-trap catalysts in car exhaust systems. In the previous Roadmap, “integration” was one of the keywords. However, this mostly referred to integration of reaction and process design in bulk chemistry. While the chemical development of multi-catalyst systems in homogeneous and biocatalysis is already underway, the engineering counterpart, (i.e. multi-reaction or multi-reactor systems) is lagging behind. That is unfortunate, as such systems would offer attractive opportunities in process intensification.

The integration of catalysts can be achieved using two different approaches. The first is the **plug-and-play or “LEGO” approach**, whereby individual catalytic systems are self-contained and modular, but nevertheless combined with other catalytic modules. Simple implementations of this concept are already being applied industrially, for example by coupling a first equilibrium reaction to a second irreversible process, which drives the first equilibrium reaction to completion. Another area that requires the integration of catalysts is the development of solar fuels, where oxidation and reduction occur concurrently, but need to be spatially separated, see also the challenges and opportunities paragraphs in Chapter 5 CO₂ Conversion and Solar Energy Storage. The overall goals of the plug-and-play approach are to expand the repertoire of viable chemical reactions, to increase product yield and selectivity, and to reduce the production of waste, thus enabling process intensification and increasing cost-effectiveness.

The second approach, which we will call the **bio-inspired approach**, is more reminiscent of how catalysis occurs in biology. There catalytic systems co-exist and influence each other, for example through feedback loops. The highly ambitious long-term goals in this approach are to build a synthetic cell and create life *de-novo*. This approach resonates with **complexity research** as it is conducted in and across many different disciplines,

including topics ranging from social networks to the research on the brain. So far, within the field of catalysis, complexity research remains underdeveloped, although momentum is gathering.

Challenges

The main challenges that need to be addressed in order to make more complex catalytic systems a reality are **catalyst and process compatibility**. A single synthetic catalyst is usually only effective under its own set of special experimental conditions and usually has limited tolerance for other chemical species in the system. Yet, building more complex systems or devices requires compatibility – ideally between different catalysts, but at least between conditions and/or process parameters.

For the “LEGO” approach there is a need for **plug-and-play catalytic modules**, whether as units that can be combined within the same homogeneous environment or separated by compartmentalization or immobilized in (micro) flow reactors. Systems may require structured reactors, in which reactors and catalysts are ideally optimized simultaneously, requiring close collaboration between chemists and engineers. It will also be important to develop and incorporate inline analytical technologies (ultrasound tomography, temperature tomography, NMR, etc.) into the reactors to be able to study (in the development phase) and monitor (in the production phase) the processes. A cascaded flow processing needs also to ensure that solvents, concentrations, ingredients, etc. are compatible with each other in what is referred to as “flow orthogonality”. Another major challenge results from differences in the rates at which catalysts lose their activity, usually through poisoning or leaching. A workable integrated multi-catalyst system will therefore have to offer the opportunity of independent catalyst-activity management.

For the bio-inspired approach, the main challenge is to achieve good **compatibility between the many different catalytic sub-processes** that occur in parallel in a single system. Nature’s solutions for avoiding unproductive interference between sub-processes is to separate them in space by immobilization, compartmentalization or steric shielding. Most catalytic sites in enzymes are inside cavities in the structure of the enzyme, while in most man-made catalysts, the catalytic sites tend to be exposed. Work has started on implementing similar immobilization strategies with man-made catalytic systems.

Opportunities for Catalysis

When combining chemical processes side-by-side (as in the “LEGO” approach) or within a single system (as in the bio-inspired approach), **catalysis is essential** as it **allows independent control over the rates at which the various reactions occur**. Such control is crucial if the various reactions are to be efficiently integrated. Without catalysis, such control is largely absent and one would be dependent on the rate constants of the various reactions. That, in turn, would severely restrict the ability to engineer well-integrated complex chemical systems. For example, a cell would not be able to function in the absence of ways to independently regulate – through catalytic processes – the rate at which the various chemical reactions inside it occur. Thus, by developing integrated catalytic systems, we will be opening up new opportunities, ranging from a more cost-efficient production of chemicals that require multiple reaction steps to functional complex chemical systems leading to life **de-novo** and cells that are completely synthetic.

Dutch Strengths in Integrated Multi-Catalyst Multi-Reactor Systems

The integration of multi-catalyst systems and the accompanying processes requires the **integration of the underlying disciplines** such as catalysis, chemistry, process engineering, biology and physics and it requires the integration of the communities that work in these disciplines. Through its national programs and events the Dutch school of catalysis has a long and unique tradition when it comes to integrating homogeneous catalysis, heterogeneous catalysis and biocatalysis with biotechnology research. Such integration at the level of communities will benefit a similar integration at the level of the actual catalysts. The Netherlands is also strong in bridging chemistry with chemical engineering and vice versa, e.g. the chemical and/or biochemical technology departments at the technological universities. A holistic approach is ultimately needed to bring innovations into practice and to ensure industrial valorization. Process-design and engineering departments such as those at the universities of Delft, Twente, and Eindhoven will play a crucial role in the end-of-the-pipe implementation, particularly for the “LEGO” approach.

Furthermore, academia in the Netherlands has internationally **leading expertise in the area of complex chemical systems**, e.g. in the Gravity programs on Functional Molecular Systems and on Multiscale Catalytic Energy Conversion, in the research initiatives in Groningen, Nijmegen and Eindhoven, and through its leading role in consecutive COST Actions on Systems Chemistry. The development of complex catalytic systems will benefit from combining the strength of the supramolecular and catalysis communities. The

first steps in this direction have already been taken in the context of the NRSCC. In the meantime, however, that program has come to an end, and we have to ensure that the momentum that had been building will be passed on to the new initiatives.

Another impetus for research on integrated catalytic systems comes from the “**cell as a factory**” **research** within BE-Basic. Finally, large chemical companies such as DSM often have highly developed competences in individual technologies such as homogeneous catalysis, heterogeneous catalysis and biocatalysis and flow chemistry, and a combination of these competences is where differentiation from competitors kicks in.

Research Areas & Deliverables

Areas of Research

The application of multi-catalyst systems and the respective multi-reaction/reactor systems ranges from a relatively straightforward extension of existing methodology, whereby the resulting system has properties that are effectively a sum of its individual components, to systems which show emergent behavior. In the latter case the total is more than the sum of its parts, and a collection of catalysts create a function at a higher level. We can distinguish between the plug-and-play or “LEGO” approach and the bio-inspired approach and define specific research areas. For the **plug-and-play approach** these lines include serial multi-step reactions in a flow setup (serial multi-device reactions) leading to specific products. The implementation of such systems requires controllable plug-and-play devices in which catalyzed reactions may be performed. Catalyst activity is independently managed for each device. The product of a single step, which is the substrate for the next step, is selectively and continuously

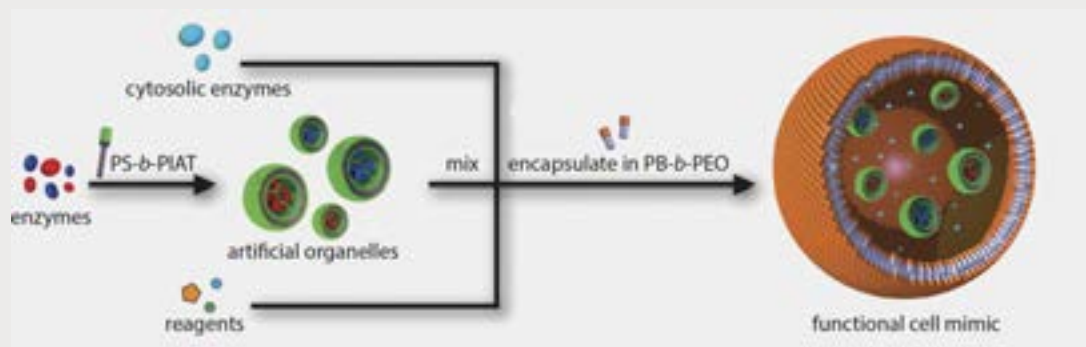
removed from the device and fed into the next unit. The development of such systems requires the input from separation technology, organic chemistry and process technology.

Two research lines may be implemented that use either the “LEGO” or the bio-inspired approach. The first line includes one-pot multi-step chemical transformations involving multiple catalysts leading to specific products. The second line involves smart catalytic systems in which the outcome (i.e. product selectivity) may be controlled by controlling the individual reaction steps or in which the activity may be controlled in time and/or space through (local) physical or chemical triggers. This requires the development of stimuli-responsive catalysts. The possibility of having dynamic variation of catalyst activity, e.g. by electronic control, may be another asset. The industrial implementation of such systems requires analytical methods that are

sufficiently fast and specific to fit their process control task. This adds analytical science to the required competencies.

For the bio-inspired approach to integration, a specific area of research is formed by networks of catalyzed reactions that are strongly interconnected and that give rise to emergent functions as they would do in biology. Here it is not necessarily the product of the reaction network but rather its functional behavior that is of interest. Such functions may include computation, autocatalysis/self-replication, oscillations, and spatio-temporal pattern formation (Turing patterns). The ultimate aim for many researchers in this field is to create life *de-novo*. Feedback loops are essential elements for advanced function and designing and engineering catalytic systems that include feedback loops is of prime importance. Internal control mechanisms in such systems will

First artificial cell with working organelle



Jan van Hest and coworkers (Peters, R.J.R.W. et al., *Angew. Chem. Int. Ed.*, 2014, 53, 146-150) used polymeric vesicles to recreate the structural design of a eukaryotic cell and its organelles. Such multicompartment structures can be made by encapsulating small porous polymeric nanoreactors inside a larger

polymeric vesicle. This system can then be used to spatially separate incompatible enzymes from each other by positioning them in different organelle subcompartments. This still allows the enzymes to function together in a multi-step cascade reaction, but without affecting the other catalysts.

Figure reproduced in adapted form from Peters et al., *Angew. Chem. Int. Ed.*, 2014, 53, 146-150, with permission of John Wiley and Sons.

rely heavily on non-covalent interactions, which means it will be important to involve the strong supramolecular chemistry community in the Netherlands in the development of this line of research.

Deliverables in 10-20 years

Plug-and-play (“LEGO”) approach

- a toolbox of plug-and-play catalytic modules in which catalysts are integrated into tailored reactors;
- several industrial (flow) processes in which multiple catalysts are integrated which enabled a more cost-effective production of (fine) chemicals.

Bio-inspired approach

- the ability to design and synthesize integrated catalytic systems exhibiting feedback behavior;
- significant steps towards the synthesis of life de-novo, in particular fully synthetic self-reproducing catalytic systems will have been made that are capable of undergoing Darwinian evolution. While the synthesis of life de-novo may require several decades, significant steps towards this tantalizing goal will have been made towards the end of the period covered by this Roadmap;
- man-made integrated multi-catalyst systems that complement current biotechnology-based processes in the production of fine chemicals. These industrial applications are appearing on the horizon, although those may well lie beyond the timescale of the present Roadmap;
- personalized medicine, where micro or nanoscale integrated systems autonomously perform in-vivo sensing, data analysis and treatment by release of specific drugs.



Fundamentals and Methodology

9

The future development of new and improved catalytic material and processes will require a methodological shift towards rational design supported by fundamental knowledge. The integration of new spectroscopic and microscopic tools along with predictive modeling strategies will allow us to design and synthesize new molecules and complex materials with structural and chemical properties that are well-defined and controlled over various length- and timescales, leading to more cost-effective and sustainable catalysts and catalytic processes. Improved fundamental knowledge of catalysts (and catalysis in general), including their functioning and manufacturing processes, will enable, among other advances, the replacement of noble, scarce, and toxic elements by more abundant and environmentally safe metals for catalysis.

Status & Challenges

Current Situation

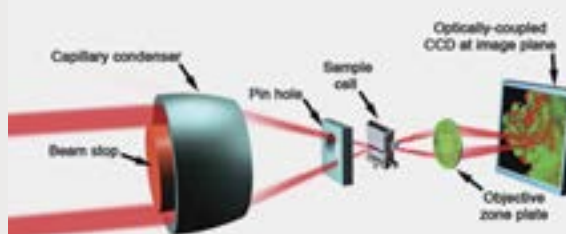
In the last decades, technological developments in the fields of spectroscopy, imaging and computational tools have provided **increasingly detailed molecular insight into catalytic reactions**, including examples of atomic descriptions of catalytic processes, making it possible to explain the reactivity observed. Despite these advances, a complete spatial and temporal description of such events is not yet possible, and new technological breakthroughs are necessary before we can observe the full “movie” of catalysts in action – a challenge for both homogeneous and heterogeneous catalysts. A new scientific and technological revolution, characterized by cost-efficient and smart chemical systems, will require a transition from explaining to predicting material-design parameters for new catalysts.

In relation to the 2001 Technology Roadmap, the subject of fundamentals and methodology was mostly examined in the ASPECT- and CatchBio-programs, in which a variety of new spectroscopic

tools were developed. This new Roadmap focuses on **introducing predictive power into catalysis** and centers on the development of new experimental tools and theoretical methodologies that will lead to the knowledge-based design of any desired catalytic system. The rational design of catalysts has historically required the study of well-defined systems to allow changes in performance to be correlated to a small set of material parameters (in heterogeneous catalysts) and molecular structure (in homogeneous catalysts). Although tremendous progress has been made in closing the gap between models and realistic systems, further studies combining theory, spectroscopy, and synthesis will be required to fully bridge this gap. This holds true for all types of catalysis. The guiding principle for the fundamental direction will be the combination of predictive molecular modeling, advanced molecular gas- and solution-phase spectroscopy, 3D atomic-resolution spectroscopy, and the capability to translate the lessons learned into the design and synthesis of catalysts and catalytic processes ranging from the atomic and molecular levels to macroscopic scales.

Nanotomography of working catalyst particles

Ines D. Gonzalez-Jimenez, working with Profs. Frank de Groot and Bert Weckhuysen, proved that individual iron-based Fischer–Tropsch–Olefins (FTO) catalyst particles can be studied by *In-situ Hard X-ray Nanotomography* at elevated temperatures and pressures. 3D and 2D maps of 30 nm resolution could be obtained and show heterogeneities in the chemical composition and pore structure of the catalyst particle of about 20 µm. (Angewandte Chemie International Edition, vol 51, 11986–11990, 2012).



Challenges

Having a fundamental understanding of catalytic processes on multiple timescales and length scales is key to identifying and overcoming the major bottlenecks to scientific and technological developments. A continuous drive to bring about improvements in the stability, selectivity and performance of catalytic systems, from laboratory to industrial levels, must therefore be supported by strong research efforts in fundamental research and in the development of novel methodologies. In this connection, we list six important challenges for fundamental research in catalysis.

Advances in catalysis, be it homogeneous, heterogeneous or biological, will require **optimal control over chemical reactions** (i.e. chemical bonds), catalytic sites in molecular catalysts, and surface structures. We need to fundamentally improve our understanding of catalysis, and improve our capability to selectively activate the desired bonds. Equally so, spectroscopy at the level of the single molecule or the single catalyst site will help us better understand the effects of catalyst ensembles.

An additional important fundamental challenge in homogeneous catalysis is to **gain control over highly reactive (hypovalent) intermediates** such as transition metal carbenoids, nitrenoids, phosphinidenoids, ketene, ketenimine, allene, nitride and oxo-complexes, and their (radical-type) analogues. These intermediates are highly relevant in a variety of C-H activation and C-C, C-O, C-N and C-P bond formation reactions (including formation of ring compounds, new polymers, building blocks for organic synthesis, etc.). However, they are often difficult to control to the desired levels of selectivity. Avoiding the use of high-energy reagents to prepare hypovalent intermediates is extremely desirable from a perspective of sustainability and efficiency. This is (at least in principle) possible by **combining catalysis with electrochemistry (catalytic**

electro-synthesis). In this way reactive (hypovalent) intermediates can be directly generated at e.g. the anode of an electrolyzer. This challenging and promising field of catalytic electro-synthesis is poorly charted, and clearly deserves more attention.

We will need to focus more on **predictive modeling** rather than explanatory modeling, translating our atomic understanding into material or process-design parameters and synthesis strategies. This will allow for atomic-scale resolution in active site design as well as 3D control of meso- and macroscale structures (e.g. through self-assembly), enabling macroscopic effects like mass transfer. This would include the development of reactions and processes that do not require functional group protection and provide a general strategy towards functional group transformation (important in biomass conversion).

In theory development, we need to take into account the **very different timescales and length scales** relevant to a proper description of catalysis, e.g. picosecond bond-making and bond-breaking events at atomic scale up to diffusion and reaction phenomena in meter-sized reactors. Complementary to theoretical research, investments are also needed in surface science, as the detailed experimental description of the atomic level provided by surface science is key to further developments in the context of new advanced materials.

Fundamental studies must concentrate both on catalysts (molecules, materials and preparation) and catalysis (activity, selectivity, stability). The role of promoters and solvent and support effects also needs to be taken into consideration. Developments towards the control of selectivity by generating second-sphere effects are particularly relevant in the context of homogeneous catalysis, where this area is still fairly unexplored.

The increasing use of high-throughput methods and tomographic techniques has dramatically increased the amount of data that becomes available per experiment. Handling this data, and **understanding complexity in catalytic systems**, such as the complex mixtures in commercial feedstocks (whether from biomass or fossil origin), is a huge challenge that will require, among other things, the development of analytical chemistry and data-handling tools beyond the current level

Opportunities for Catalysis

An improved fundamental understanding of catalysts and catalytic reactions will unlock many new opportunities for the application of catalysis and lead to new catalytic routes to new molecules. These advances are key to – and will go hand-in-hand with – the necessary shift towards a more sustainable and economically valuable catalysis, from academic research to industrial application levels.

A prerequisite for tackling the challenges defined above is the further **development of sophisticated characterization tools**, capable of mapping activity and chemistry at the surface. This includes the integration of spatially and temporally resolved spectroscopy with microscopy methods, as well as real-time spectroscopy. Time-resolved spectroscopy in particular is key to be able to fully describe catalytic events such as photocatalytic processes. In other cases, completely new tools for probing molecular catalysts and catalyst surfaces will be required. Examples of these new tools are free-energy lasers and THz excitation, which can be used to probe femtosecond dynamics in single bond-breaking events. Synchrotron sources present the opportunity to characterize structural and electronic changes down to the lifetime of reactive intermediates in the pico- and nanosecond regime. It is fundamental for the development and improvement of (homogeneous) catalysis to determine the reaction mechanisms via reaction

kinetics and diverse spectroscopic studies in order to identify reaction intermediates.

An important aspect to consider in the context of the **theory and modeling of realistic catalytic systems** is whether physical insight is possible from studying realistic systems or model systems under realistic conditions. The catalytic truth at atomic scale may be hidden under various “onion rings” of effects that govern the process at larger length scales or higher temperatures, like mass transport and diffusion effects. In biocatalysts, small changes remote from the active site can induce significant improvements. With the newly developed tools, these distant interactions will help to improve all types of catalysis. At the same time, experimental validation should be done in realistic systems, bridging the temperature and pressure gaps.

Understanding realistic complex systems will tremendously speed-up progress in all fields of catalysis. As an example: recent developments in bioinformatics provide the opportunity to extract and predict the reactivity and structure of complex enzymes, combining data from gene, protein and x-ray databases. Translation of concepts like these to homogeneous and heterogeneous catalysis will unlock completely new possibilities.

In order to develop **catalysts based on abundant first-row metals**, we need to understand the reactivity of these catalyst complexes in detail, including their radical-type behavior. After all, these complexes can be based on non-innocent and innocent ligands, resulting in complementary reactivity. These ligands have more of a general applicability and can thus minimize the metal costs through lower catalyst loadings. We should find a way to reduce the time for ligand development via modular approach and in particular using computation, which should become the main tool for ligand design instead of the present broad screening approach. In addition, the development

of metal-free catalysts should be further explored by developing new catalyst systems and concepts. In these particular systems, traditional spectroscopic techniques (IR, NMR) are less conclusive, and require less established and often more difficult to interpret characterization tools, such as EPR and Mössbauer spectroscopy, as well as X-ray absorption and emission techniques as a complement to the development of new synthetic procedures.

The increased understanding we gain from characterization and theory should give us an opportunity to combine our insights and to gain improved control over the synthesis of new catalysts, both heterogeneous and homogeneous and their design from the atomic scale upward. For heterogeneous catalysts, atomic-scale precision should be combined with the 3D meso- and macroscale location of components to create realistic, strong and stable new catalysts. The capacity to build well-defined systems via nanomanipulation and the possibility of performing catalysis on a single nanoparticle are identified as long-term development opportunities. The controlled synthesis of hybrid materials, which

combine homogeneous building blocks with heterogeneous surfaces, will give a powerful impulse especially to the fields of cascade reactions and solar fuels.

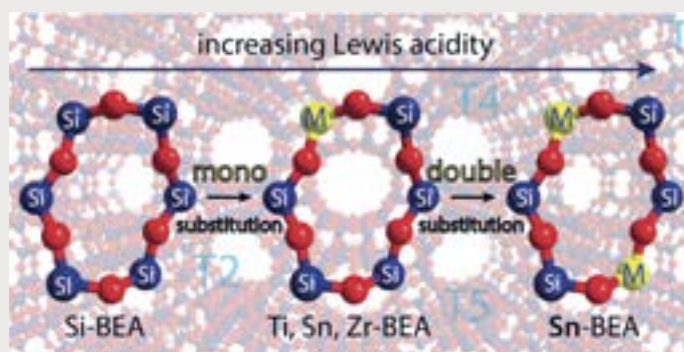
Finally, chemoselectivity needs more attention. Now that we are contemplating complex feedstocks, reaction cascades, one pot syntheses, CO₂-activation and systems catalysis, the rational design of targeted catalytic functionalities that do not interfere with other functionalities will be important. Catalysts would be desirable that can selectively convert a single functionality in complex, multifunctionalized molecules.

Dutch Strengths in Fundamentals and Methodology

A fundamental understanding catalysis at all scales is one of the true strengths of Dutch catalysis research. In heterogeneous catalysis, control over the size and morphology of nanometer-scale active clusters had been proven for various systems, yet

Modeling Lewis acidity in Beta-zeolites

Gang Yang, Evgeny Pidko and Emiel Hensen studied the siting of heteroatoms in zeolite BEA and the resulting Lewis acidity with periodic density functional theory (DFT) calculations. They found that the Lewis acidity of substituted zeolites strongly depends on the crystallographic location of the heteroatoms. The presence of paired lattice sites in Sn-BEA zeolite substantially enhances Lewis acidity, which clearly distinguishes Sn-BEA from its Ti- and Zr-substituted analogues (J. Phys. Chem. C, 2013, 117 (8), pp 3976–3986).



the (self-)assembly of these clusters into macroscopic systems remains an interesting challenge. In homogeneous catalysis, concepts from nature's catalysts, such as the capacity of methane monooxygenases to convert methane to methanol, have been a proven source of inspiration and at the same time a challenge to aim for.

Dutch research on theory and modeling has traditionally been strong but now risks losing its place at the forefront. Strong fundamental tool development is still available in Amsterdam (the ADF package of the Amsterdam Centre for Multiscale Modelling), and efforts to strengthen the modeling expertise are in progress at other universities. These efforts should be stimulated and further expanded.

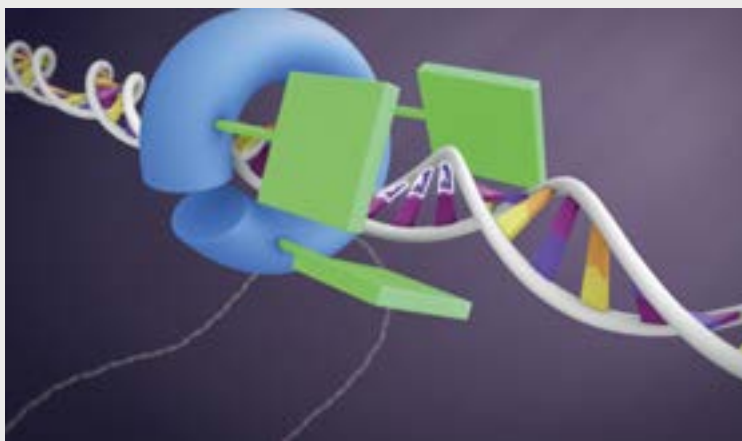
The development of homogeneous catalysts for the bulk and fine chemical industries, including the

application of such systems, is represented at a high level in the Netherlands.

Atomic-resolution spectroscopy under industrial operating conditions has undergone considerable development in the past decade. Many of the new tools were developed and first applied in the Netherlands. Various light and X-ray tomography tools have been developed here to study catalytic processes *in operando*. Further improvements in spatial and temporal resolution, labeling techniques, and chemical imaging are required to improve our fundamental understanding of real-life catalytic systems. Large research infrastructural facilities are either present in the Netherlands (NMR, HFML, TEM) or scientists have good access to international facilities that are not available nationally (synchrotron and neutron sources, FELs). Research in general would benefit from setting up a national platform for (the integration

Processive catalysis

Compared to traditional, so-called distributive catalysis in which substrate and catalyst only meet once, processive catalysis is more efficient because the reactants associate and remain connected, facilitating multiple round of reactions before they separate. Stijn van Dongen, working with professors Roeland Nolte and Alan Rowan, developed a C-shaped biohybrid catalyst that operates in this fashion (Van Dongen et al., *Nature Chemistry*, 5, 945-951 2013). It binds to a DNA plasmid and while moving along it cleaves the chain at specific locations (AAA sites) in a processive manner. When the loading of the catalyst to the DNA chain is prevented by a peptide the mechanism changes from processive to distributive because the cleavage reaction can only occur randomly.



A biohybrid protein clamp (blue) provided with 3 manganese porphyrin catalysts (green) glides along a double stranded DNA chain, while cutting it at AAA sites (picture ICMS Animation Studio, TUE)

of) experimental techniques. Catalysis research as a field where many of these experimental techniques come together can play a pioneering role here.

Finally, the Dutch school of catalysis is known for its holistic approach to catalysis, which combines the aspects stressed above: theoretical understanding, spatially and temporally resolved spectroscopy at high resolution, and 3D atomic design and synthesis. The strong cooperation and close relationship between industrial and academic research in the Netherlands provides the ideal framework for the transition from understanding small-scale model systems to understanding large-scale real-life systems.

Research Areas & Deliverables

Areas of Research

In the context of this Roadmap for Catalysis, it is clearly the intention that developments mentioned here in “Fundamentals and Methodology” will benefit all other topics that have been identified as priorities in the preceding chapters. Addressing the previously indicated challenges will require concerted and multidisciplinary actions that will take advantage of the existing strengths in the Netherlands and strengthen those areas that are less explored, as in the case of Theory and Modeling. A set of key research focus areas is discussed below:

Optimal control over chemical systems and reactions

A detailed understanding of chemical kinetics and reactivity, focused particularly on structure- activity relationships, will be the basis for the rationalization of reaction mechanisms, leading to an improved design of catalysts and catalytic processes: higher efficiency, stability and selectivity. Simultaneously,

the ability to design, prepare and characterize new materials with 3D control at atomic or molecular resolution and at various length scales must be developed. New concepts in ligand design must be explored to allow for catalysis with more abundant, first-row transition metals. The molecular chemistry of these catalysts and metal complexes needs further development. The availability of characterization tools for a diamagnetic system like Pd has led to a good understanding of this system, but the organometallic chemistry of for instance Fe is hardly explored. Apart from activity, stability of this type of catalyst needs to be examined. The development of fundamentally new homogeneous catalysts needs attention, e.g. in the field of organocatalysis, but also photo-redox catalysts, and molecular redox catalysts. The latter may find more use when electrical energy would be more abundant through solar conversion routes.

In order to improve the catalytic transformations in particular in homogeneous catalysis novel synthetic methods for ligand preparation as well as predictive modeling for achieving sophistication in ligand engineering in order to develop ligands with desired chemo-, stereo- and regioselectivity and high values of TOF and TON are required. Another important aspect would be a development of heterobimetallic catalysis in order to provide cooperative catalysis coming from two different metals. Only a few examples are known, mainly due to the lack of corresponding ligands to bind to different (soft and hard) metals.

Predictive modeling

Theory, multiscale modeling, and computational chemistry together form one of the pillars of the strategy proposed in this Roadmap for Catalysis. The development of descriptive and predictive methodologies based on input from new spectroscopic tools will provide a much more detailed insight into the parameters that play a role in catalysis. Research in this area will benefit from

development in the adjacent fields of complexity and big data research. Rather than simply understanding such parameters, the focus will now be on predicting which set of conditions will be most suitable for a given catalytic process.

Understanding complex and real systems

Enhanced spectroscopy and microscopy on realistic systems, incorporating 3D atomic-resolution characterization techniques, in situ and ex situ methodologies, broad time resolution, and data processing and analysis tools (e.g. dephasing, multivariate procedures) will allow the identification of the key descriptors that can serve as the basis for design rules for new catalysts and molecules. This field is strong for heterogeneous catalysis, but needs development for homogeneous systems, especially with respect to homogeneous catalysis with first-row transition metals.

In this perspective, the use of computational tools to better understand spectroscopic measurements which are otherwise difficult to interpret (e.g. EPR, Mössbauer, XAS/XES spectroscopy) in catalysis research is also important. This should again be concerted with the development of theoretical methods that incorporate more realistic, more complex systems, moving away from small molecular models, model surfaces, clusters and single molecules.

Deliverables in 10-20 years

- Computational methods that account for the complexity of chemical/catalytic processes on various timescales and length scales;
- A transient view of catalysis that accounts for out-of-equilibrium processes, instead of the current steady-state view;
- Precise control of morphology, composition and defect structure, leading to influence optical, electronic and catalytic properties on multiple scales;
- A toolbox to translate chemical descriptors of catalysis and catalysts into predictors and design rules for new molecules and synthetic methods;
- The science-based development of highly stable catalytic molecules and materials with self-repair and self-assembling properties;
- Mechanistic insight by combining spectroscopy with computational spectroscopy;
- Control and efficient generation of highly reactive (hypovalent) catalytic intermediates;
- The precise control of selectivity in synthesis and catalysis, including regulation mechanisms to accommodate changes in reaction conditions (e.g. as observed in natural photosynthesis);
- The targeted activation of specific catalytic sites and the control of reaction speeds and mechanisms, allowing for a cost-effective utilization of catalyst materials and an efficient replacement of noble metals by cheaper and more abundant materials;
- Novel synthetic methods for ligand preparation as well as predictive modelling for achieving sophistication in ligand engineering in order to develop ligands with desired chemo-, stereo- and regioselectivity and high values of TOF and TON;
- New homogenous (organo)catalysts for photo-redox catalysis, molecular redox catalysis and challenging group-transfer reactions;
- Chemoselective catalysts that can selectively convert a single functionality in complex, multifunctionalized molecules.

10

Annexes

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71

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Abbreviations

ACTS	Advanced Chemical Technologies for Sustainability	NGO	Non-Governmental Organization
ADF	Amsterdam Density Functional package	NIMIC	Nano-IMaging under Industrial Conditions
ASPECT	Advanced Sustainable Processes by Engaging Catalytic Technologies	NIOK	Netherlands Institute for Catalysis Research
BBE	BioBased Economy	NMR	Nuclear Magnetic Resonance
BE-Basic	Biotechnology based Ecologically Balanced Sustainable Industrial Consortium	NRSCC	Netherlands Research School Combination Catalysis
CatchBio	Catalysis for Sustainable Chemicals from Biomass	NWO	The Netherlands Organisation for Scientific Research
CCS	Carbon Capture and Sequestration	OCM	Oxidative Coupling of Methane
COST	European Cooperation in Science and Technology	PHAs	Polyhydroxyalkanoates
DECHEMA	DECHEMA Society for Chemical Engineering and Biotechnology	PO	PolyOlefin
DFT	Density Functional Theory	PPP	Public-Private Partnership
DNA	Deoxyribonucleic acid	PV	PhotoVoltaic
DPI	Dutch Polymer Institute	RAFT	Reversible Addition-Fragmentation chain Transfer
ECN	Energy Research Centre of the Netherlands	RSC	Royal Society of Chemistry
EPR	Electronic Paramagnetic Resonance	SET-LRP	Single-electron transfer living radical polymerization
EPSRC	The Engineering and Physical Sciences Research Council, UK	SMEs	Small and medium-sized enterprises
EST	Eni Slurry Technology	TASC	Technology Areas for Sustainable Chemistry
EU	European Union	TEM	Transmission Electron Microscopy
FCC	Fluid Catalytic Cracking	THz	TeraHertz
FDCA	2,5-FuranDiCarboxylic Acid	TOF	TurnOver Frequencies
FEL	Free-Electron Laser	TON	TurnOver Numbers
FTO	Fischer–Tropsch-to-Olefins	VFA	Volatile Fatty Acids
GDP	Gross Domestic Product	VIRAN	Industrial Advisory Board of NIOK
GECATS	GERman CATalysis Society	VNCI	Association of the Dutch Chemical Industry (Vereniging van de Nederlandse Chemische Industrie)
GHG	GreenHouse Gas	XAS	X-ray Absorption Spectroscopy
HFML	High Field Magnet Lab	XES	X-ray Emission Spectroscopy
HSE	Health, Safety, Environment		
IBOS	Integration of Biosynthesis and Organic Synthesis		
ICCA	International Council of Chemical Associations		
ICHEME	Institution of Chemical Engineers		
IEA	International Energy Agency		
InSciTe	Institute for Science & Technology		
IOP Catalysis	Innovation-oriented Research Program Catalysis		
IR	Infra-Red		
LCA	Life-Cycle-Assessment		
MOF	Metal-Organic Framework		
MTO	Methanol To Olefins		
NCCC	The Netherlands' Catalysis and Chemistry Conference		



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