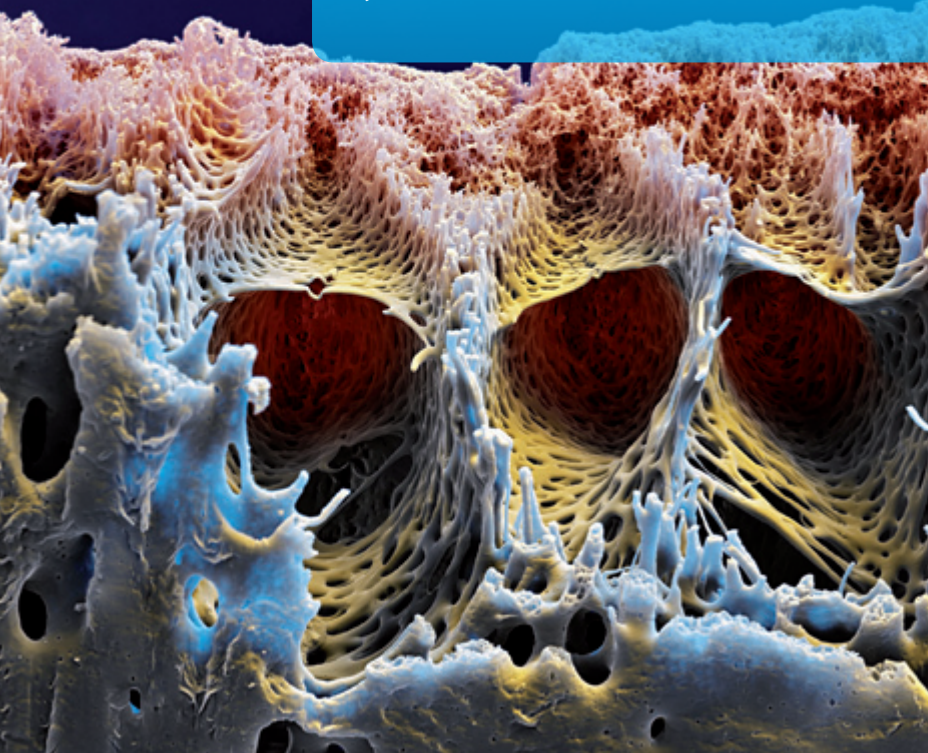


SUPPLEMENT TO THE
ROADMAP FOR CATALYSIS RESEARCH IN GERMANY

CATALYSIS

beyond the roadmap

June 2012



supported by



Catalysis beyond the roadmap

For drawing a roadmap, at least the general lay of the land needs to be known. Information is needed on where there are mountain ranges, rivers, coastlines, cities and so on. Only then it is possible to plan an itinerary from here to there. For roadmapping in science, analogous considerations hold: in order to do a reasonable foresight of the future development, a certain degree of maturity is required in a field. Otherwise the general direction in which a field will move is difficult or even impossible to predict. Many of the most exciting discoveries occur in uncharted land and open new horizons, and exploring the completely unknown is often most rewarding.

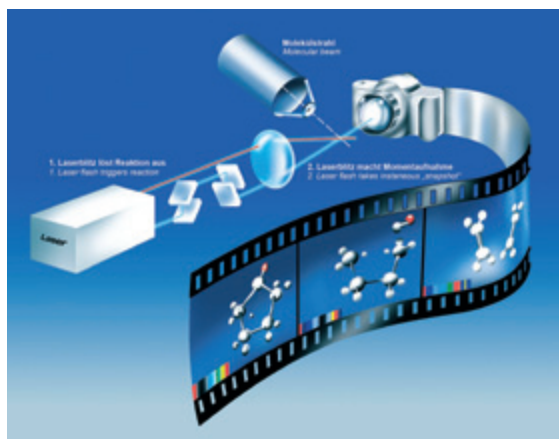
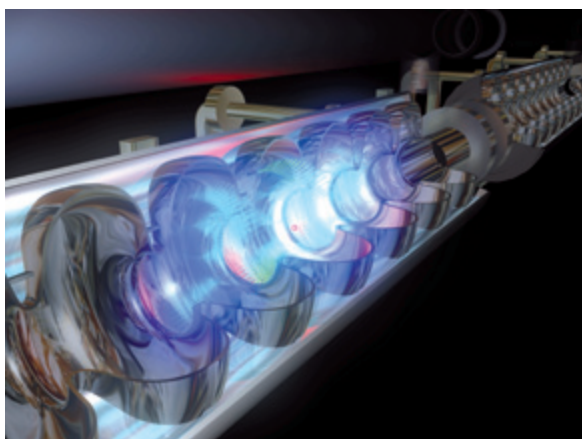
Science holds completely unforeseen discoveries, these can never be predicted. These fields are not – and cannot be – within the scope of this chapter on catalysis beyond the roadmap. However, there are areas in catalysis in which too little is known for a true roadmapping, with clear steps to be taken to reach a specific goal. Of these fields, however, we already have a glimpse, and they appear so interesting that it is worthwhile to at least make an attempt at describing the general features of the landscape in order to draw a roadmap later. These fields will be sketched in the following.

Molecular movies: the catalytic event at the molecular level

In section 7.3 the power of in-situ and operando spectroscopies has already been highlighted. Many techniques which were thought to be impossible to use under in-situ conditions, such as electron microscopy or XPS, are now close to applicability at atmospheric pressure – even if this is certainly not routine, yet, and will not become so for the next decade or so. However, there are methods on the horizon which may lead even further: some analytical techniques could eventually reach a level of sophistication by which bond breaking and bond making at the single molecule level could be studied.

Two groups of techniques appear to be especially suitable for this purpose. These are atomic probe microscopies, and the range of pump-probe and structure analytical techniques which could become available at the next generation of X-ray sources, i.e. the X-ray free electron lasers.

Atomic probe methods allow single molecule detection routinely nowadays. With more advanced techniques, such as single molecule surface enhanced Raman spectroscopy, it is already possible to study electron exchange dynamics between single adsorbed molecules and a sur-

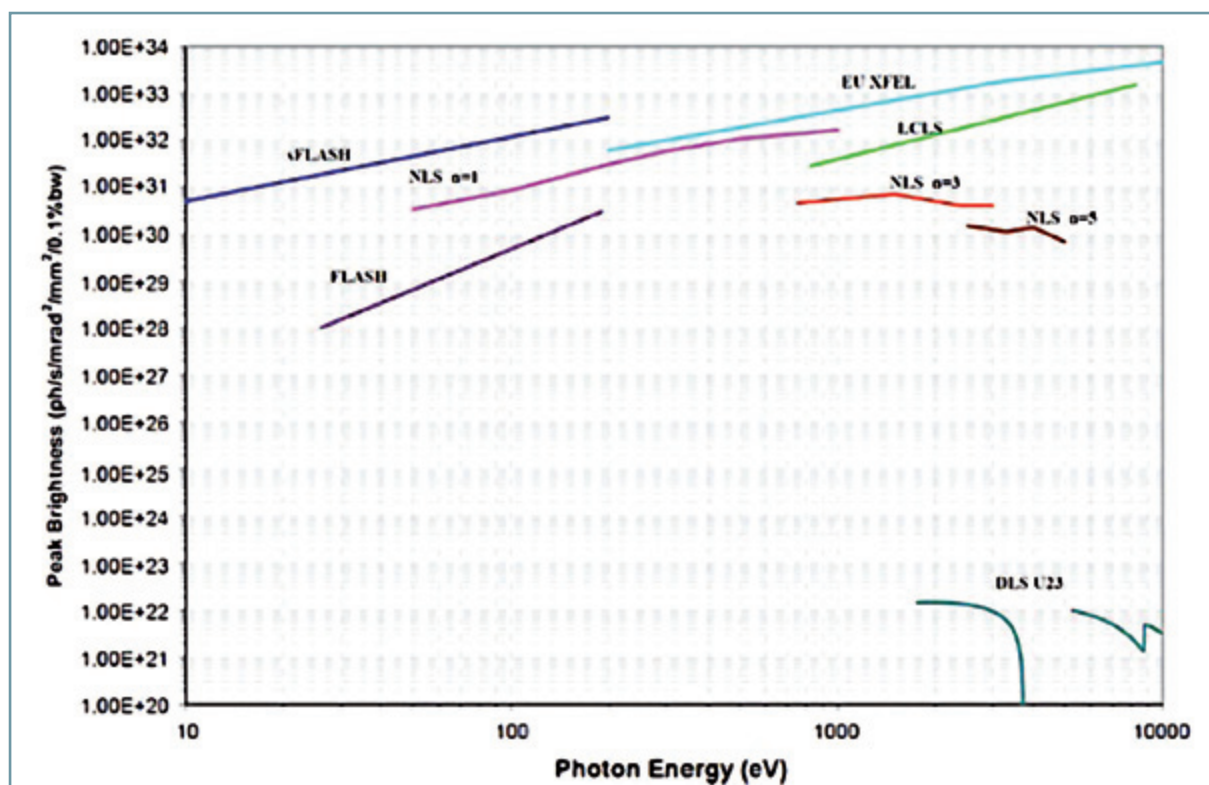


Left: artists impression of an X-ray free electron laser, right: schematics of molecular movie to be obtained in a pump-probe experiment (both images from DESY)

face. It has also been shown for several cases that it is possible to directly observe global electronic states by STM methods which in some cases can directly be associated with orbitals. The strength of individual bonds between surface and adsorbed molecules can be probed by different atomic probe methods, in the easiest way by just pulling off the tip from an adsorbate covered surface and measuring mechanical forces. This suggests that the analysis of single catalytic events on surfaces could come into reach in the future.

X-ray free electron lasers could provide exciting opportunities for catalysis research in the future. Free electron lasers produce X-ray light pulses which have similar properties as laser pulses in the visible range, i.e. coherence, extremely high brilliance, and very short pulse length. The brilliance exceeds that of conventional synchrotron light by many orders of magnitude, while the pulse length can be as short as femtoseconds. The most advanced X-ray free electron lasers are in operation since 2009 at Stanford (Linac Coherent Light Source, LCLS) or scheduled to begin operation in 2014 at DESY (XFEL). For experiments at X-ray free electron lasers, some of the underlying physics is still unclear. Molecules which are exposed to such intense radiation will certainly be destroyed. However, if

experimentation is sufficiently fast, the fingerprint of the molecule can be taken before the degradation process has begun, on a scale of pico- down to femtoseconds. It may thus become possible to obtain snapshots of chemical reactions of single molecules, and possibly of the reactions of molecules on surfaces. In pump-probe type measurements, a visible or X-ray pulse could trigger an event in a molecule or on a surface, and an X-ray probe pulse could then be used to reveal *structural* information in an EXAFS or diffraction-type experiment. We are still quite far away from such measurements. First results on LCLS have demonstrated that structures of individual viruses could be imaged at a resolution on the order of 10 nm, and structure solution for photosystem I was possible for very small, not well crystallized nanocrystals. There are still many physics questions to be solved, and it will probably take some time, before relevant data on catalytic questions can be delivered by free electron X-ray lasers. However, the first results from LCLS are encouraging, and after 2014, when XFEL at DESY will begin operation, a new level could be reached. Especially important for the German catalysis community is the fact that FEL science is strongly driven by German groups working at the Center for Free Electron Laser Science (CFEL), a joint initiative of DESY, the Max-Planck-Society and the University of Hamburg.



Energy and brightness for various light sources. DLS stands for the range covered by a standard undulator beam line at Diamond Light Source (from: J.P. Marangos, Contemporary Physics 52, 551 (2011))

Imperfection is key: controlling the defect structure of solid catalysts

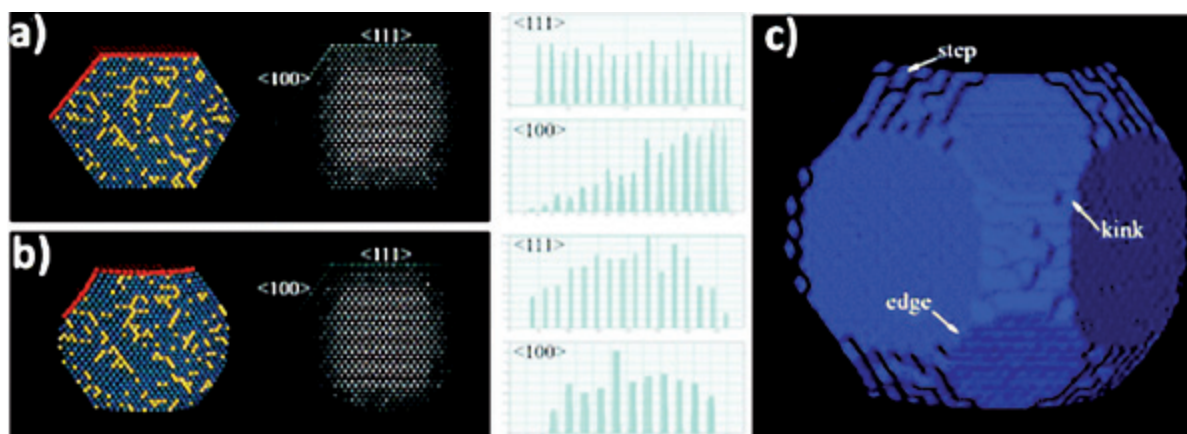
There is ample evidence that the defect structure of solid catalysts is decisive for many catalytic reactions. Many types of defects are candidates for high activity sites, such as fault lines, step sites on surfaces, oxygen vacancies, or strain in nanoparticles, to name just a few. The catalytic activity often seems to be governed by the non-equilibrium structure of solids. Controlling this non-equilibrium structure is thus of the highest importance in catalysis, with “controlling” being important with respect to the creation of such structures, analyzing the presence of such structures, and maintaining the non-equilibrium state under reaction conditions. This field thus links to the previous section, where the catalytic event at the molecular level – which may be a defect site – is discussed.

It is known in heterogeneous catalysis that the pathway leading to a particular catalyst can be highly important for catalytic activity, even if afterwards nominally identical catalysts are obtained. This is in many cases the effect of the defect structure, which is formed differently by different synthetic protocols. The defect structure, however, is typically not adjusted by design, but empirically optimized. Even if one could rationally control the defect structure during synthesis of a catalytic material, this does not guarantee that this structure is maintained during the catalytic reaction which often proceeds at high temperature, tending to equilibrate the defect concentrations.

Advances in different fields could help in the future to control the defect structure in a rational manner. Here different lines of research come together: advanced, atomically

resolving techniques, such as aberration-corrected electron microscopy, in-situ techniques for the analysis of catalysts under working conditions, and synthetic methods which could allow to maintain the defect structure by encapsulation, controlled doping, use of epitaxial mismatch, and others. In many cases, the problems are actually related to the ones encountered in the microelectronics industry, at least in case of semiconductor-type catalytic materials. Techniques developed in that field could possibly be leveraged into the field of catalysis, at least in the analysis of defect structures.

In section 7.3 it was already mentioned that in-situ techniques to monitor catalyst synthesis need to be developed. If these techniques revealed the defect structure, which develops during synthesis, this could provide a handle to rationally control this property of a solid catalyst, which in turn could improve the performance, at least, if this structure could be retained under reaction conditions. Innovative synthetic methods are required to stabilize the relevant defects. In section 7.1 it was already mentioned that nanostructured catalysts – non-equilibrium structures in themselves due to the small particle sizes – appear often suitable for the stabilization of such structures. However, there could also be other techniques to stabilize the relevant defects under reaction conditions, such as the use of stable matrices, which shape the active phase, or the combination of thermally stable structures with less stable structures generated by techniques such as atomic layer deposition. A balanced interplay between synthesis and sophisticated ex-situ and in-situ analytical techniques is required in order to make progress in this field, in addition to advanced theoretical approaches.



Distribution of Pd and Au in a PdAu nanoparticle, as analyzed by modelling of aberration corrected STEM images. The presence of the second metal induces defects which could be responsible for the enhanced catalytic activity (from D. Ferrer et al., *J.Mater.Chem.* 18, 2442 (2008)).

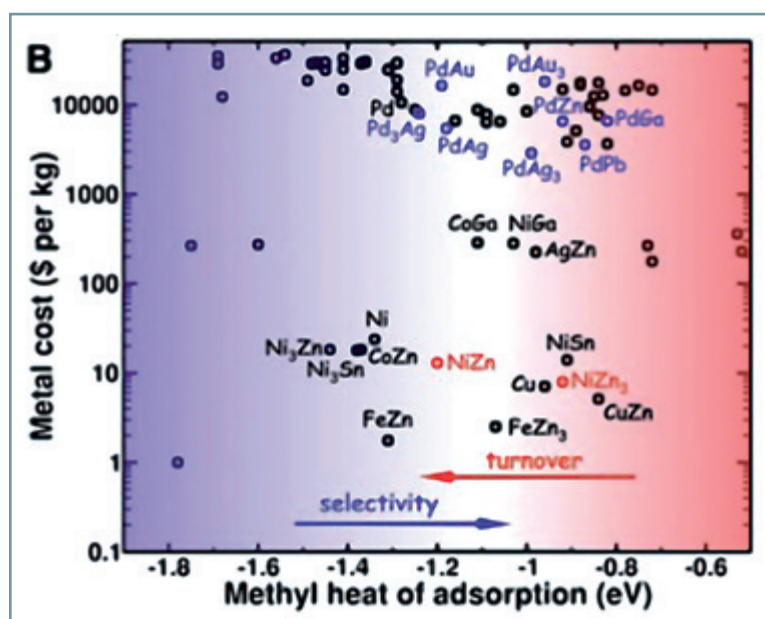
Handling complexity: theoretical description of the catalyst under working conditions

Theoretical chemistry has reached a very high level of sophistication. In catalysis, quantum chemical calculations are now sufficiently powerful to go beyond the ex-post rationalization of experimental findings; in fortunate cases, such calculations now have indeed predictive power. The understanding of catalytic turnover in molecular systems is constantly pushed forward with improved methods for the elucidation of electronic, steric, and geometric effects. For solid catalysts this has become possible, since for selected problems the systems can be described reasonably well with one parameter, such as the d-band center or the energy of the formation of oxygen defects. Such single descriptors can then be correlated with catalytic performance, and volcano-type plots result.

system. This means that also the complete surrounding of the catalytic site has to be considered. Such a multiparameter description of a realistic catalytic situation is currently out of the reach of quantum chemical calculations, the reaction path is typically described as a series of metastable states. In spite of the tremendous increase of computing power, the system size which would need to be considered is still far too large. Progress in hardware and in the algorithmic implementation of code on massively parallelized processor architectures will alleviate these problems to some extent. However, there is also a need for conceptual innovations in the approaches to make larger systems traceable and to include hitherto neglected effects in powerful theoretical approaches, such as the inclusion of dispersion forces in DFT codes which has recently been achieved.

Programs such as the various Exascale Computing Initiatives, where a co-development of hardware and software

in massively parallelized (on the order of 10^7 processors) computer systems is planned, and the constant innovation in the theoretical concepts for tackling complex quantum chemical problems could provide the catalysis community with the means which would allow the search for better catalysts based on theoretical calculations. Theory will be able to direct experimental efforts, and the constant interplay between experiment and calculation will help to further hone the methods required on both sides.



Calculated methyl heat of adsorption as a descriptor for selective acetylene hydrogenation versus cost of the catalyst metals (from F. Studt et al., *Science* 320, 1320 (2008))

Such methods have proven to be remarkably successful for many cases, but they reach their limits, if more complex, multi-step reaction sequences should be understood, since they can typically not be captured anymore in a single parameter. Unfortunately, such reactions are often the most relevant ones in technical catalysis. Moreover, for a realistic description it is highly desirable to reach a quantum chemical description of a catalytic reaction, including the catalyst, as a true non-equilibrium

complex biological systems where a number of different enzymes act together in a concerted and synchronized fashion to catalyze a series of reaction events, which eventually lead to a certain target molecule. In such cases one needs more than just the catalysis of a series of individual reaction steps; the molecule to be processed must be passed on from catalytic center to catalytic center without undergoing side reactions or being released into the medium before the reaction sequence is completed.

Catalytic machines: transport of molecules from catalytic site to catalytic site

Most present day chemical catalysts are single molecules or more or less complex surfaces. This also holds for many enzymes, where a single transformation is being effected. However, there are more

Such enzyme complexes are the result of millions of years of evolution, and mostly, these complexes do not operate autonomously, but require the presence of the organism which provides the framework for the action of this machinery.

However, it would be extremely interesting, initially certainly only from a scientific point of view, but in the distant future eventually possibly also under a commercial aspect, to be able to design and produce such complex catalytic machines by synthetic methods. The resulting systems do not need to be modelled after their biological counterparts – one may rely on completely novel principles, possibly even has to, because it would be too difficult to provide the entire cell machinery which is required to have an enzyme complex operating.

First successful attempts along such lines have been described, such as the polybutadiene epoxidation catalyst which is “clamped” on the polybutadiene polymer strand. In this case the control is achieved by the rotaxane-like structure of the system which keeps the catalyst threaded on the polymer strand. Movement along the strand is, however, random, so that the catalytic action here is not combined with a controlled movement.

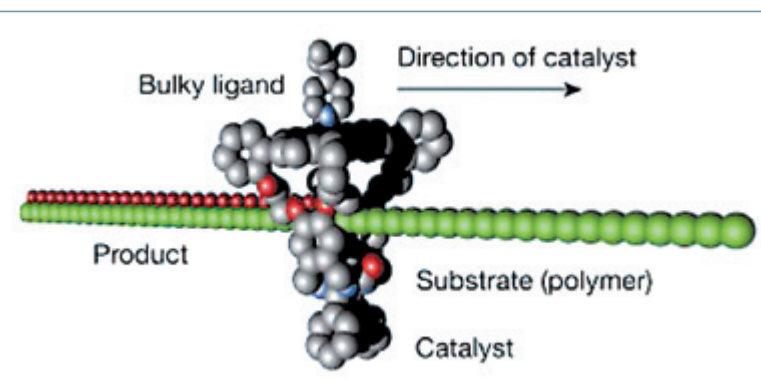
Directed movement of surface-bound entities has been reported already. Molecular rotors and systems, where linear directed movement is achieved under consumption of energy, have been described. With this, the major elements for the construction of a catalytic machine are in place. If one would fix different catalytic functionality at defined locations along the track of a molecular motor, these different functionalities might act in a sequential fashion on one molecule bound to the motor. Initially, the synthetic effort to realize such a system would most prob-

ably be tremendous. Moreover, often not many repetitive cycles are realized, because the systems degrade. However, efforts in this direction could lead to understanding the principles and patterns, along which catalytic machines could operate. In addition, one has to keep in mind the analytical challenge which needs to be met in order to prove that a designed catalytic machine is indeed operating according to the design. Nevertheless, in spite of these challenges, the construction and realization of catalytic machines - either along the design principles found in nature or following novel concepts - appears to be a fascinating intellectual challenge. Key components seem to be available, the decisive challenge is their assembly into a functional system.

Metabolic engineering: whole organism catalysts

Enzymes are an exciting class of catalysts, and all organisms rely on enzyme catalysis, as well as some industrial production processes. Enzyme catalysis is well established in various fields of industrial production, and also enzyme engineering, mostly done by various methods of directed evolution, has a firm place in the toolbox of chemists. Many enzymes or enzyme complexes could also be considered as catalytic machines, as discussed in the previous section. However, the concept of catalysis may be pushed even further: one could consider also whole organisms as catalysts, even if this means stretching the limit of the concept. We are already nowadays using living organisms for chemical production, the best known example probably being the production of ethanol from sugar using yeasts. However, for most chemicals which we are using, there are no native organisms which provide them at all or at least cost efficiently at high yield.

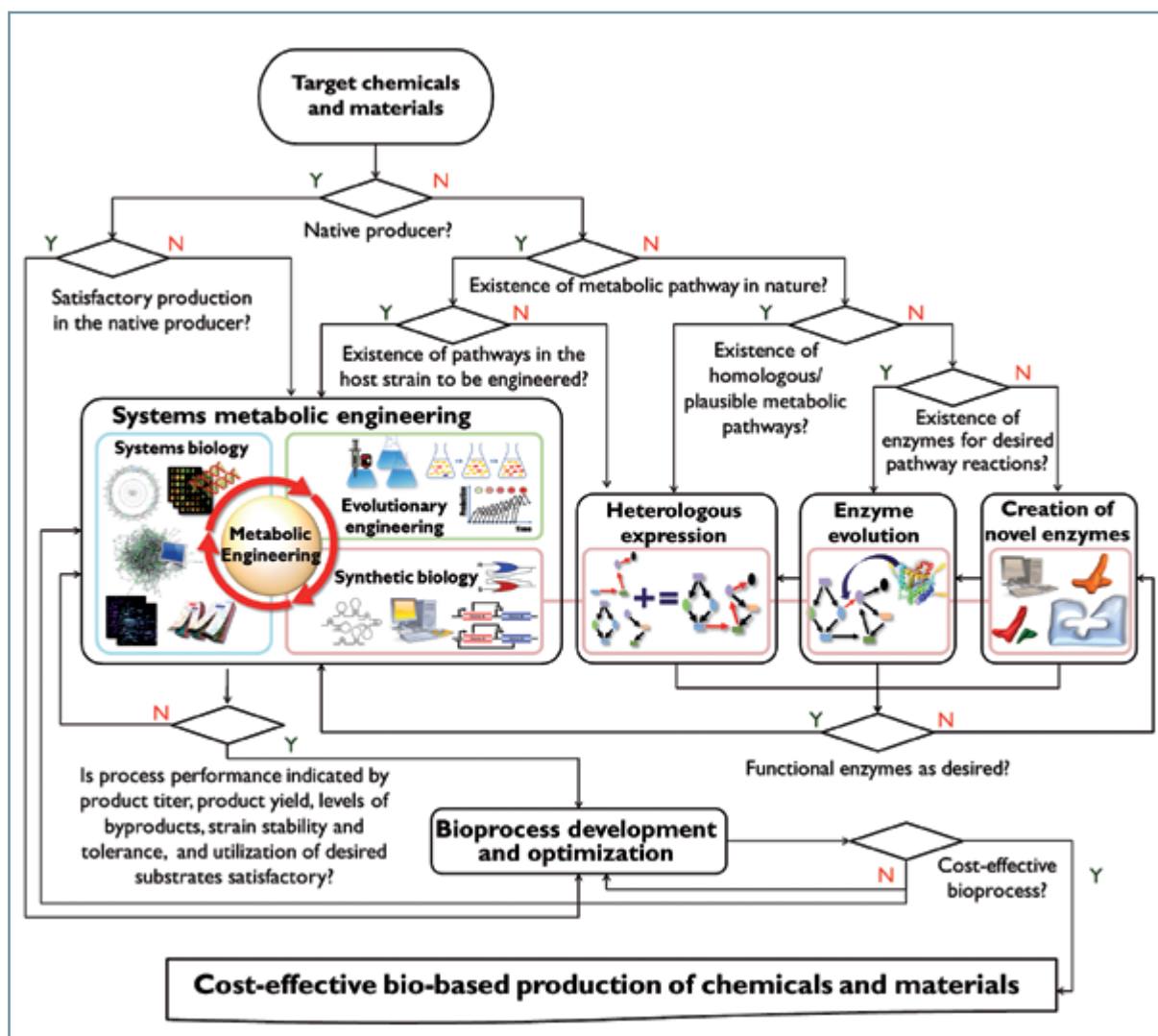
Here metabolic engineering starts: it first relies on the analysis of metabolic pathways for the production of a target metabolite and the mathematical modelling of such pathways, with one of the goals being the identification of constraints which limit production. In a next step, genetic engineering methods are used to modify the pathways in order to relieve the constraints and to create genetically modified organisms which are more efficient in producing the target metabolite. There are several successful examples where this has indeed been achieved. However, in many cases the organisms that produce the target molecules are not easily cultivated or even can not be cultivated at all. In such cases, the metabolic apparatus used for the expression of a certain metabolite has to be transferred into an organism which allows cultivation.



Schematic representation of a manganese-based rotaxane-like epoxidation catalyst acting on a polybutadiene thread (from P. Thorardson et al., *Nature* 424, 915 (2003)).

There is a number of platform organisms which are useful for this purpose, such as *Escherichia Coli* or *Saccharomyces Cerevisiae*. However, in many cases the productivities are relatively low, and the concentrations eventually reached are on the level of 10 mg/l. While this is not sufficient for the production of bulk chemicals or intermediates, for specialty chemicals or drugs such concentrations are on a relevant scale. Metabolic engineering requires a detailed understanding of metabolic mechanisms and the interplay of the different processes in the cells to be used as the production unit. Typically, manipulation of just one pathway has negative consequences for the organism, so

that they do not grow and eventually die, and thus, only in fortunate cases can single manipulations be successful. If one induces production of certain chemicals, it could also be necessary to increase the tolerance of the cells against the target metabolite, since they may in fact be cell toxic. There are thus many questions to be solved before the use of whole organisms as the “catalyst” is generally applicable. However, the potential of such technologies appears to be tremendous, and production of chemicals in engineered organisms may at least replace part of chemical production in the future.



Schematic view of systems metabolic engineering process for the production of chemicals and materials (from J.W. Lee et al., Trends in Biotechnology 29, 370 (2011)).

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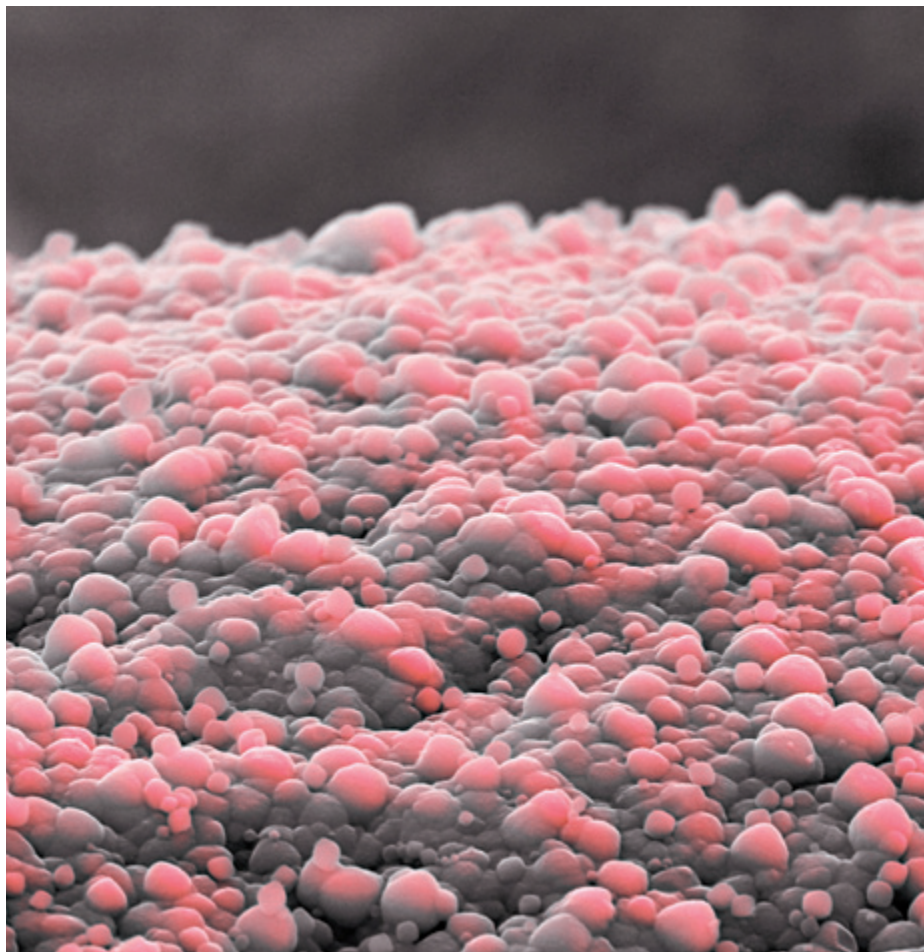
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