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Robert Schlögl

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The solar refinery

Robert Schlögl

Abstract

Renewable energy utilization in grid dimensions cannot be achieved without shadow storage options due to the overall volatility of the primary electricity generation. Whereas in the near future this will be covered by fossil capacity in modern gas and coal power stations, new storage options based on artificial energy carriers will be needed in the medium future beyond the next decade. Such storage options will for medium-term storage times be chemical storage as well as for many mobility applications requiring compact power. Several options exist for such solar fuels which all are based upon solving the central issue of water splitting to arrive at solar hydrogen as platform system. Reacting solar hydrogen with CO_2 from fossil or biological sources to conventional or non-conventional energy carriers can generate solar fuels for end applications using existing technologies for distribution and usage. These reactions will be carried out in solar refineries. The intended use of biomass as natural storage form of solar energy is insufficient for the global energy demand considering the priorities of food production and ecosystem stability.

Introduction

The energy system is a fundamental characteristic of a human society. All its individual and collective actions require the availability of free energy in various forms (mechanical, chemical, electrical). The sum of all man-made inorganic energy inter-conversion processes reaches at the end of the first decade in the 21st century the same dimension[1] as the biological processes needed to generate the food for mankind. Both process groups amount to about 15% of all biological solar energy conversion on the planet earth. It is obvious that we are dealing with enormous dimensions that are difficult to comprehend, as they are so much larger than our individual frame of dimensions. In the following we discuss a few aspects of these dimensions using the example of the German energy system as the necessary data are well accessible[2] and its absolute size of about 1% of the global energy system is in suitable dimension.

The German "Energiewende" in the aftermath of the Fukushima events is a highly popularized impulse[3] on the future of an energy supply system. It comprises the termination of nuclear power generation within 10 years leading to the necessity to replace about 25 % of the German power consumption of about 600 TWh by alternative sources. This by itself was not a difficult task as within one month after the decision the contribution of nuclear power fell from about 420 GWh on 01.02.2011 to below 100 GWh on 23.05.2011 (day of nuclear moratorium 15.03.2011) (source: BDEW, "Auswirkungen des Moratoriums). The replacement came from extended use of fossil fuels and to a minor extent from a switch of net power exports to power imports much in the same way as in Japan the fast phasing out of nuclear power within one service cylce of 13 months caused an increase in fossil fuel consumption. In Germany this trend leads to increased emission of 60 – 100 million t CO_2 per annum depending on the fuel mix between coal and gas.

The Energiewende is thus partly in conflict with the German national plan for a change of the entire energy system issued in 2010[4]. In this plan it is stated that the total German CO_2 emission should fall between 2010 and 2035 from about 1000 million ton to 265 million tons. Electrical power generation, the subject of the Energiewende has a 50% share on the total emission. This should be achieved by a massive implementation of renewable energy and a smaller contribution from increased energy efficiency through various measures but mainly by strong reduction of house heating following improved building insulation. In terms of relative contributions to primary energy carriers the situation is expected to develop as shown in Figure 1:
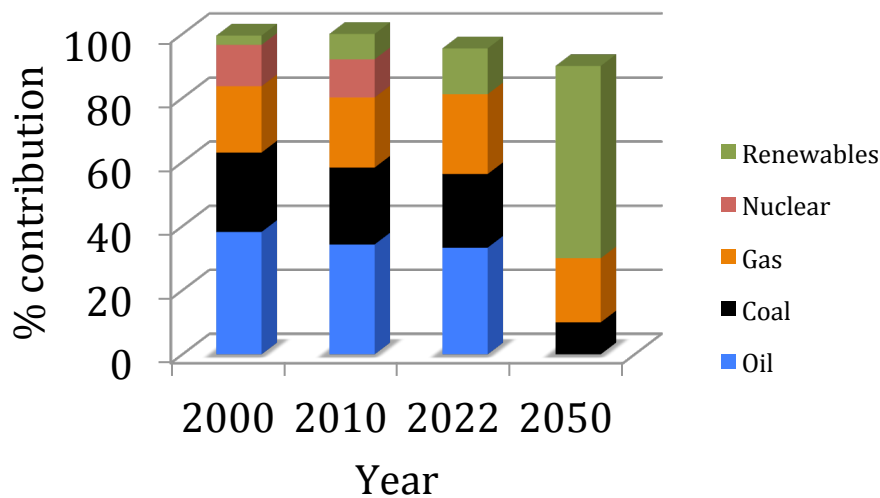

Figure 1: Relative total primary energy input into the German energy system. The values in 2022 relate to the completion of the "Energiewende", the data for 2050 for the completion of the National Energy Concept. Source: bmwi[2]

It is obvious from Figure 1 that achieving the ambitious goal of the National Energy Concept will require a deep-reaching change of the whole energy system and not only the replacement of nuclear energy in a given system. This qualifies the Energiewende indeed as an initial step rather than the great change in the energy system. The values for the year 2022 indicate that the political concept assumes a combination of 3 factors for replacing the nuclear energy: increased energy efficiency in parallel with more renewable energy generation and some additional power generation through gas combustion. In the following 35 years the contribution of renewable energy is expected to rapidly increase and to replace all oil and most coal.

In order to estimate the dimension of changes necessary it is instructive to study the distribution of absolute primary energy consumption in Germany as indicated in Figure 2.
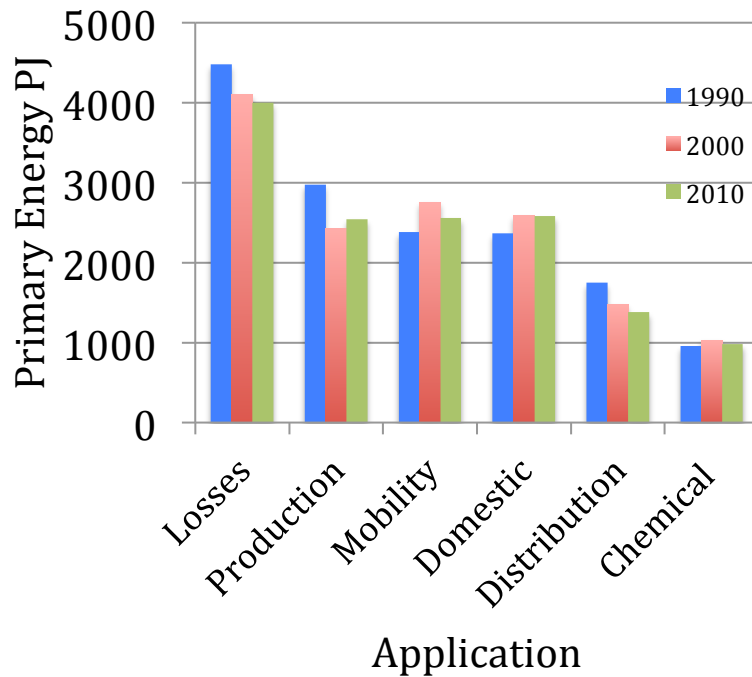
Figure 2: Distribution of primary energy streams into key application areas for Germany. Source: BMWI database 2011[2].

The energy conversion losses are by far the largest sink of primary energy followed by 3 almost equal areas of industrial production, mobility and transport and domestic energy consumption. Distribution of goods and services and the use of fossil carriers as chemical feedstock are slightly minor applications. The temporal evolution shows some changes following the industrial change with the unification in 1989 and a change in lifestyle following this event. We see very little energy saving or effects of energy efficiency increase that may well be hidden by rebound effects of increased mobility and more spacious housing. The apparent contradiction between assumed increased energy efficiency also "felt" by increasing changes towards a more energy-efficient lifestyle and the data in Figure 2 becomes clearer when the correlation between the German GDP and the CO_2 emission (being proportional to the fossil energy input) is considered. In Figure 3 it is shown that the total GDP inversely scales with CO_2 emission supporting apparently the energy saving trend. If, however, one correlates the total CO_2 emission with the changes in the production sector one finds the expected positive trend: more production means more primary energy use and hence more CO_2 emission. The trend inversion in Figure 3 is a clear sign of the strong contribution of non-production economic activity to the GDP.
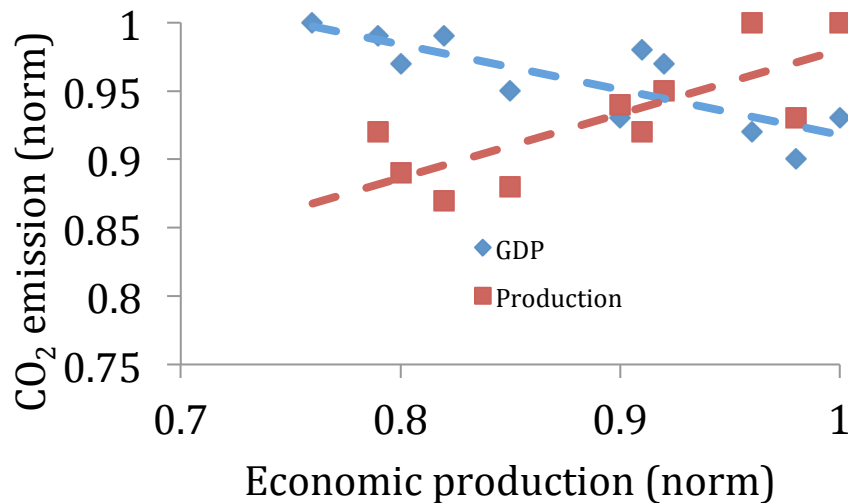
Figure 3: Relation between CO2 emission of Germany and its economic activity. The normalized values are given for the whole GDP and for the production sector only. Source: BMWI database 2011[2].

These coarse considerations indicate that energy systems[5-7] are interconnected in complex manners with multiple non-scientific aspects of utilization, generation and distribution. Simple extrapolations of "trends" into evolutionary targets for individual technologies contributing to an energy system are dangerous and misleading. It is the role of politics to define global evolutionary targets for an energy system such as to be compatible with climate protection targets[8] or to refrain from nuclear energy options. Great care should be exerted when these macroscopic targets are underlined with microscopic targets delineating development avenues for individual and innovative technologies. On this level insufficient fundamental or technical information may lead to inadequate priorizations or posteriorizations of technical options and generally precludes grassroots innovation that may lead to completely unexpected solutions. The evolution of biofuels[1, 9, 10] in different parts of the world are such an example as well as the quite specific expectations of the German energy concept that were overruled within a few months by the exit decision from nuclear power. Unrealistic high expectations in the energy saving potentials of a society without severe modifications of economic[11] or behavioral boundary conditions may also prove detrimental.

At this point we try defining the term "energy system[1, 12-14]". From the perspective of a scientist or engineer the energy supply chain from resources via distribution to application is merely a sequence of process steps of energy conversions. The free energy stored in an energy carrier is converted to other energy carriers or to mechanical/electrical energy. The challenge herby is to use a minimum number of steps to minimize the losses of free energy to the universal heat sink and to likewise minimize such losses within every step. We accept that it is impossible to convert energy without losses and that the usefulness of thermal energy is related to its difference in temperature with respect to the environment of the process.

Within this realm a very large number of processes were suggested with few of them found their way to relevant technology. Non-technological influences served as selection pressures and have thus to be considered as elements of the energy system in a more

complete sense. The non-scientific elements of an energy system are depicted with the here relevant scientific/technical elements in Figure 4.
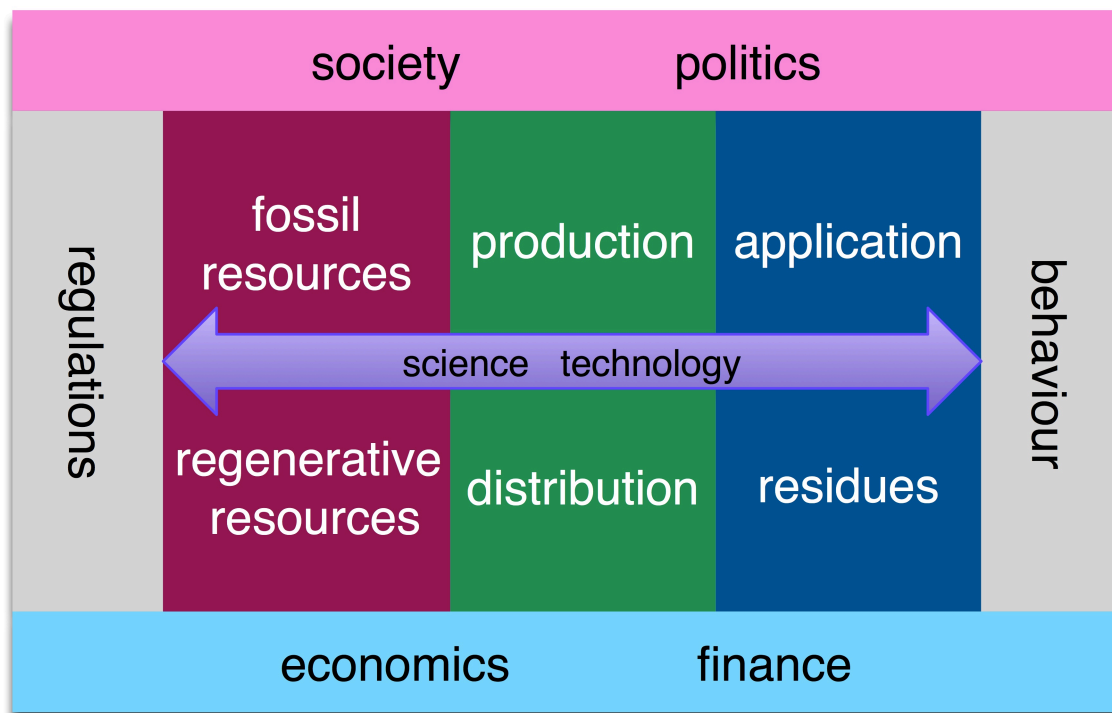

Figure 4: Scientific and non-scientific elements of the energy system. Multiple interfaces and control loops exist between the key elements. Science and technology are the enabling elements for all energy processes and additionally serve the important purpose of informing decision makers about necessary regulatory and behavioral boundary conditions.

It becomes evident that any meaningful treatment of science and technology for the energy system must be in contact with the non-scientific aspects. Science and technology further must transport its insights to those responsible for decision-making. This is clearly true for the aspects of implementing ready technologies. It is required in addition already at the earliest stages of fundamental scientific knowledge in order to account for the request of modern societies to be "knowledge societies" in which all members participate in detailed decisions on the functioning of the society. As energy supply in all its form is the cross-sectional enabling basis of all individual and collective activities of men it may be concluded that the evolution of the energy system is one of the central activities of organizing a society.

Keeping this broad view it is the intention of the present book to cover a tiny fraction of the scientific ground necessary for converting the present fossil-based energy system into one where regenerative primary energy is the main source of free energy. The following text thus concentrates not on recommendations of how to perform the Energiewende. It rather focuses on the contribution that chemistry can make to the evolution of the energy system. This contribution is twofold acting either on energy efficiency strategies of existing processes or providing solutions for the energy storage challenge being an essential ingredient into regenerative energy systems.

2. The role of chemistry in the energy challenge

This capacity of chemistry arises from the functions of chemistry being the science of inter-converting the structures of molecules and materials. All these inter-conversions are governed by the laws of thermodynamics requesting that all such processes are associated with irreversible losses of free (valuable) energy to the heat bath of the universe (not useable). Minimization of these losses through optimization of the pathway of transformation and through the optimization of functional properties of materials is one of the grand challenges of chemistry. A platform technology and science within chemistry to achieve this is the understanding and mastering of catalysis. Both our technological world of fuels and materials and nature with all its complex processes of life use this universal concept for controlling energy profiles and pathways of chemical transformations.

Catalysis[15] is the science of controlling the course of chemical reactions through managing the structure of transitions and intermediates on the pathway from educt to product systems. It uses functional materials called catalysts that bind in highly specific forms to reacting species and so control their reacting structures. These catalysts can be of the same phase as the reactants (homogeneous) or of a different phase (heterogeneous). Biological catalysis is a special form of homogeneous catalysis operating in the very restricted parameter space of life and using highly complex catalysts called enzymes.

All forms of catalysis contribute to the operation of energy systems. This is true at present as it will be in the future. All fossil fuels were generated by biological catalysis as biomass. After its death this biomass was converted by a sequence of biological (homogeneous) and geochemical (heterogeneous) reaction sequences into the present energy carriers. It is noted here that the formation of oil seemed to have occurred only once in geological times as is apparently not a continuous process. If we have consumed all oil[16] it will not be renewed by known to occur reactions. The utilization of fossil carriers in boilers (coal) or refineries (oil, gas) requires again heterogeneous catalytic processes. The conversion of chemical feedstock (see Figure 2) (all fossil) into the many thousands of materials we are using in modern life is also achieved by a combination of heterogeneous and homogeneous catalytic processes. Catalytic processes also support the final liberation of CO_2 from these molecules and materials at the end of their lifespan. Many of them occur unintentional during combustion through impurities or material-reactor interactions. In short, our existing energy system as well as much of our future energy system will require catalysis both for operating the relevant processes and for producing the required materials for energy conversion devices. Figure 5 indicates the universal role of chemistry[17] in the energy challenge both for efficiency optimization and for novel processes.
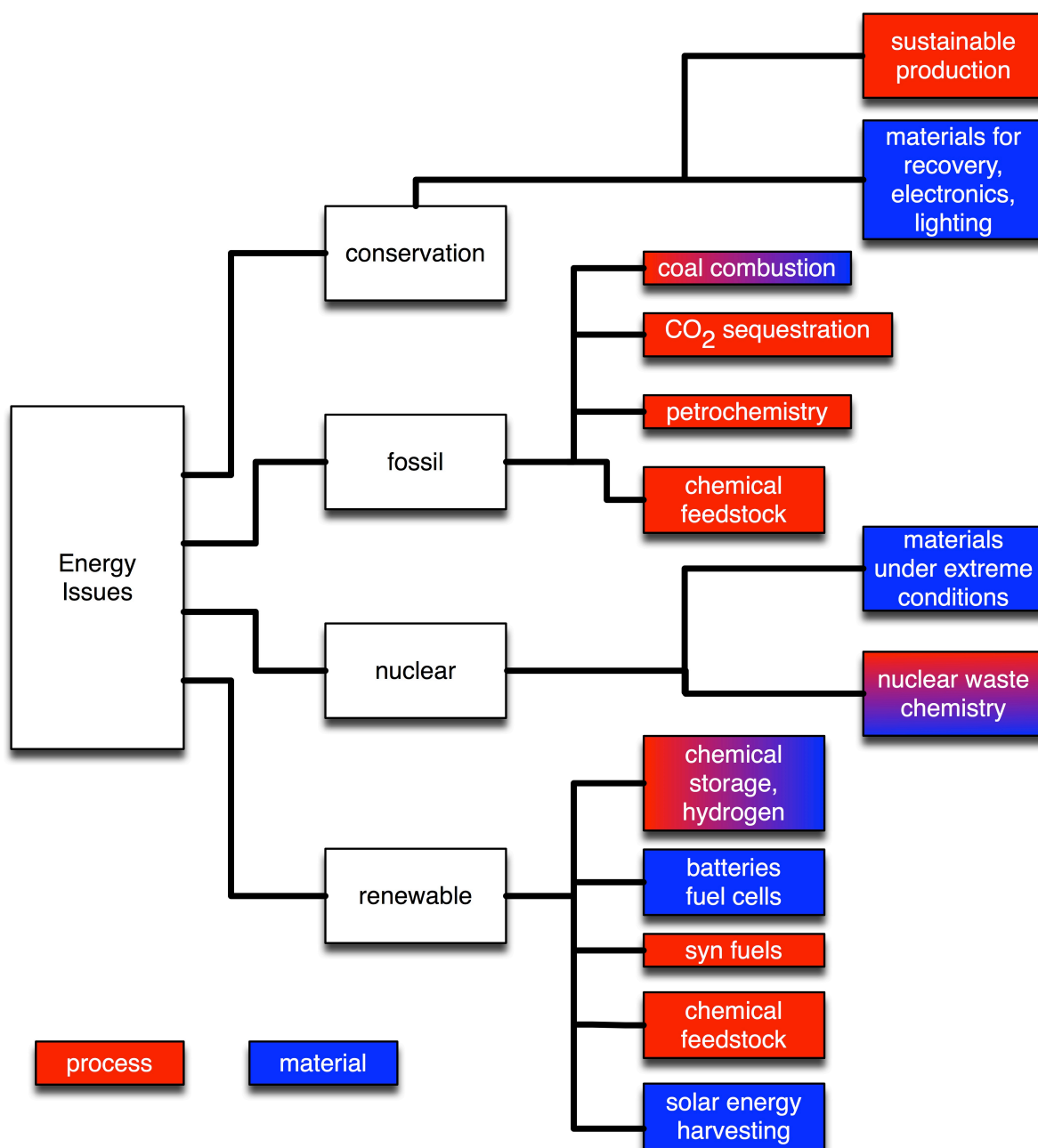
Figure 5: Chemistry is a platform science in the energy challenge. All major areas of energy conversion and use requite materials or processes provided by chemistry.

It is evident that chemistry stands at the center stage when it comes to optimization of the use of fossil energy as well as when it comes to solving the energy storage issue at large scales. It is one purpose of the following chapters of the book to provide insight into the methodologies and concepts of how chemistry can perform these tasks. If it would become apparent that chemistry is indeed a central science for addressing the energy challenge then the book is a success. It seems unclear to many how many chemical issues are hidden behind energy conversion and energy utilization being often deferred to engineering sciences.

For the sake of completeness it should be stated that increasing energy efficiency is to significant extent not to be left to chemists increasing the energy efficiency of chemical

processes; this reservoir of saving potentials is being used already[18] since a long time and all easy steps have been taken in the interest of optimizing the production in chemical industry. The much larger portion of energy saving strategies has to come from behavioral changes in energy utilization. Besides the easy steps such as house insulation also more difficult steps such as optimizing the energy efficiency of individual mobility are relevant. Also strategies of goods logistics and production are optimized for economic and taxation processes but not for energy efficiency which is counteracted by multiple transportation subsidies. These examples indicate that multiple considerations stressed in Figure 4 outside of chemistry or science greatly affect our ability to design the changeover from fossil sources.

3. Chemical reactions and catalysis

Physical chemistry is the science that describes the course of a chemical reaction. We have a solid foundation in the theoretical description of chemical reactions. Reactions occur under the rule of thermodynamics that defines equilibrium states where in a closed system (no changes in the number of molecules) no net reaction occurs. In an open system with continuous changes of the number of molecules (flow) this state equals to a maximum conversion level that cannot be exceeded at given conditions. An example of such a system is the synthesis of ammonia[19] that is at technical reaction conditions heavily limited by equilibrium conversion.

The theory of chemical kinetics describes reactions in a multi-dimensional landscape of hills and valleys given by energy as function of the atom coordinates of the reacting system. A simplified energy profile occurs when the energy change is mapped against the reaction coordinate describing in single number the changes of atom coordinates of the reacting system. For a very simple reaction the formation or cleavage of a single bond between two entities (atoms, molecular fragments) the resulting profile may look as shown in Figure 6.
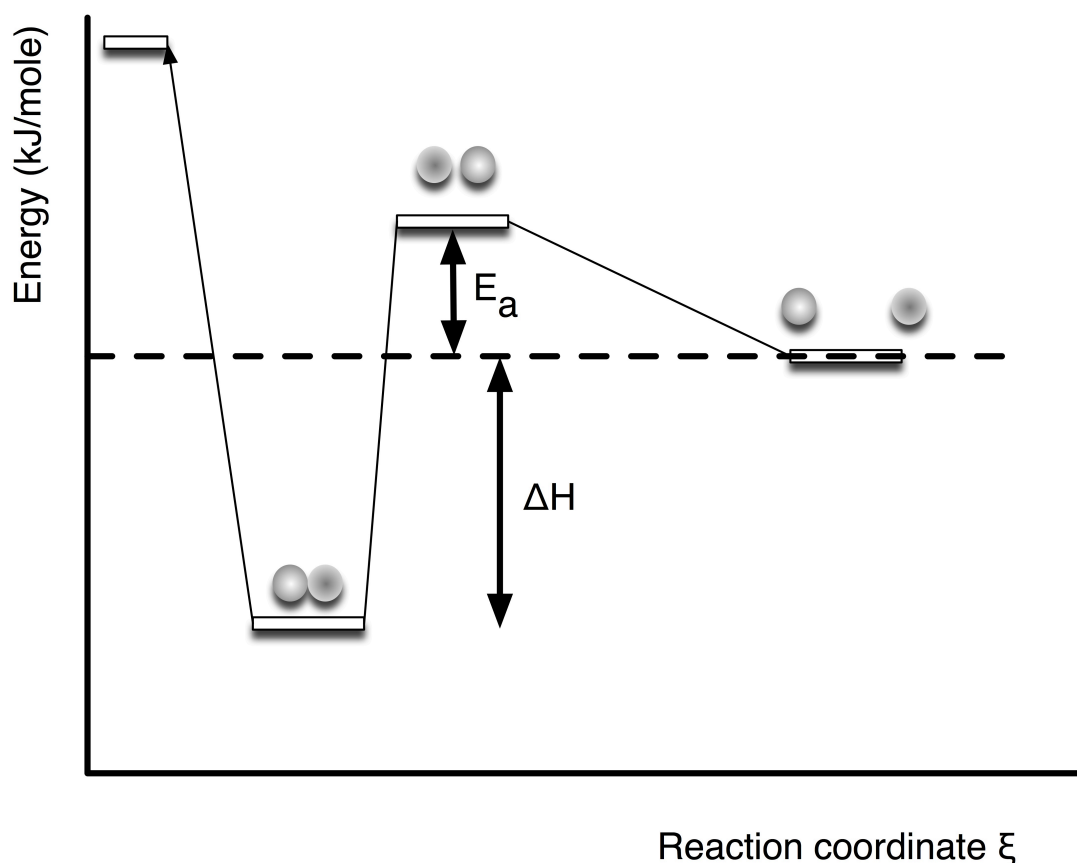
Figure 6. Reaction profile of a single elementary step. The thin lines between the energy levels are guides to the eye and do not indicate the actual course of the changes of atomic coordinates.

The process in Figure 6 is called an elementary step as it refers to the change of one single chemical bond. The energy level of the non-reacted components (educts) is defined as relative zero point of the energy scale (dashed line in Figure 6). We see that approximation of the reactants first requires energy (the activation energy E_a) as the electron clouds are repelling the bodies. At a critical distance called the bond distance the electronic systems interact quantum chemically and form a chemical bond whereby the bond energy is liberated. If we try to compress the system further the total energy is rapidly increasing as the repulsion of the core electron systems of the atoms begins to dominate. The quantity ΔH is the enthalpy change of the process that is related through the second law of thermodynamics to the free energy change of the reaction.

The activation energy can be interpreted as resistance of the system to undergo a reaction, the enthalpy change is related to the extent to which the reaction can occur. In the present context it is important to note that chemical reactions that generate free energy from reacting energy carriers with oxygen (combustion) occur with large free enthalpy changes and thus always run to completion. This is unfortunately not the case for energy storing reactions in which CO_2 is reacted with a primary energy carrier such as hydrogen to form an energy storage molecule. These reactions that require the addition of energy both in form of heat flux from the environment and in form of chemical energy of the primary energy storage molecule are strongly limited by equilibrium conversions and require special measures such as removal of the product from the reaction system in order to run to significant conversions. This is illustrated in Figure 7 for the relevant example of hydrogenation of CO_2 to methanol[20].

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$$
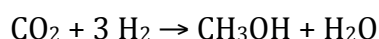
This reaction can also be considered as to occur from a first step of CO_2 reduction to CO followed by the methanol formation from CO being the more facile reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$
$$CO + 2\ H_2 \rightarrow CH_3OH$$
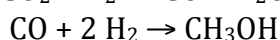
The Figure 7 indicates the maximal methanol yield as function of temperature for various mixtures of CO_2/CO at 50 bar pressure. We see that indeed severe limitations exist for CO_2 hydrogenation unless extremely efficient catalysts are found that can operate at low temperatures. Such systems are presently unknown[21-23] as we operate at typically 523 K.
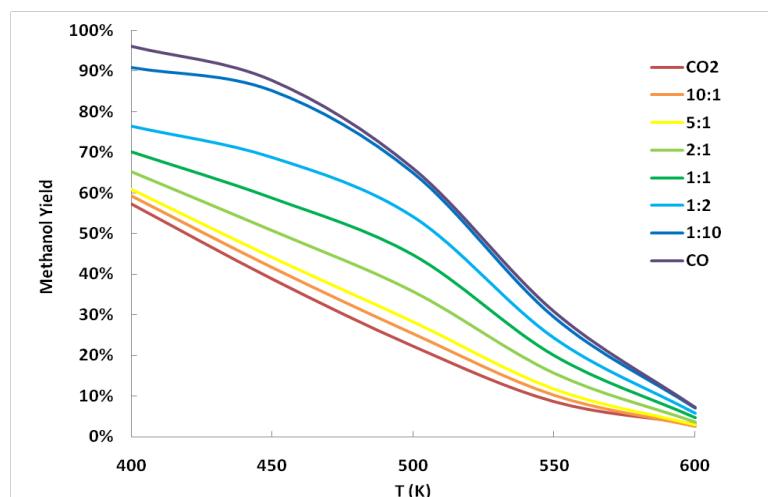

Figure 7: Equilibrium calculation for the hydrogenation of CO_2 to methanol at 50 bar pressure. The parameter is the fraction of CO in CO_2 facilitating the hydrogenation.

Without going into the details of thermodynamics here it should be noted that for chemical energy storage reactions the enthalpy change is not the relevant quantity as we are interested in the amount of work that can be done with a given amount of chemical energy storage material. This useful work is defined by the free energy and realistically by the exergy[1] of a process that relates the free energy to the actual process conditions. The free energy is independent from these conditions and thus the relevant quantity for scientific discussions, the exergy is clearly related to specific realizations of a process.

Catalysis is changing the course of a reaction by modifying the path of the system through the energy hypersurface (the energy profile as function of all relevant atomic coordinates). This is achieved by creating activated complexes between the reactants and a functional material called catalyst. The elementary step reactions change under the influence of a catalyst but not the overall energetic difference between educts and products. This is equivalent to stating that a catalyst changes the velocity of a chemical reaction but not the maximal extent to which it can occur

The statement is easy to understand when the reaction has only one product (or set of products). Typical examples are combustion reactions[24, 25] where always CO_2 and water are the final products. As molecules with many atoms (such as hydrocarbons) cannot combust in a single elementary process (not even methane) there is always the chance that several pathways may lead to several products even when then less than the

maximal energy is gained from the process. A typical example is the formation of CO as toxic byproduct of combustion.

The prototypical situation is shown in Figure 8. Here we see that an initial molecular mix has several possibilities to react. In synthetic chemistry we are usually interested in target molecules that are intermediate[26-29] in energy with respect to the thermodynamic most favorable reaction product of an educt mix. An example would be the formation of an olefin target molecule from an alkane feedstock molecule accessible by oxidative dehydrogenation with oxygen. The driving force of such a reaction would be production of the stable leaving group water as second product besides the target molecule. The undesired reaction would be the combustion of the alkane to CO_2 (and water).

In practice reaction starts by an initial activation of the educt that may represent a high hurdle[30] as the educt is a stable molecule. The system then finds a low barrier to the undesired reaction and a higher barrier to the desired one that looses kinetically against the faster undesired reaction. The result is a low selectivity to the desired product. Catalysis can now interfere (see Figure 7) by changing the reaction coordinate of the activated intermediate[31] such that the easy pathways to the undesired process is less accessible for only a small extra cost in activation energy. Then the process will slow down in velocity but gain substantially in selectivity.

The "secret" of the action of the catalyst is that by forming an activated complex with the activated reactant it changes the molecular structure of the reactant such that the undesired easy reaction path becomes unattractive. It is the specificity of the chemical bonding between substrate and catalyst that exerts the beneficial effect. In many catalytic processes an additional effect greatly changes the reaction rate: If more than one reactant is necessary then not only atoms but also electrons and atomic fragments need to be exchanged. A catalyst can provide the separation of these elementary steps in space and time. It can first activate one reactant and store the activated species at a reaction site for later use with the other reagent and it can lend and receive back redox equivalents (electrons) to participating species[32]. In this case the catalyst changes profoundly its own structure and it must be designed such that it can regain its initial structure when the catalytic turnover is completed.
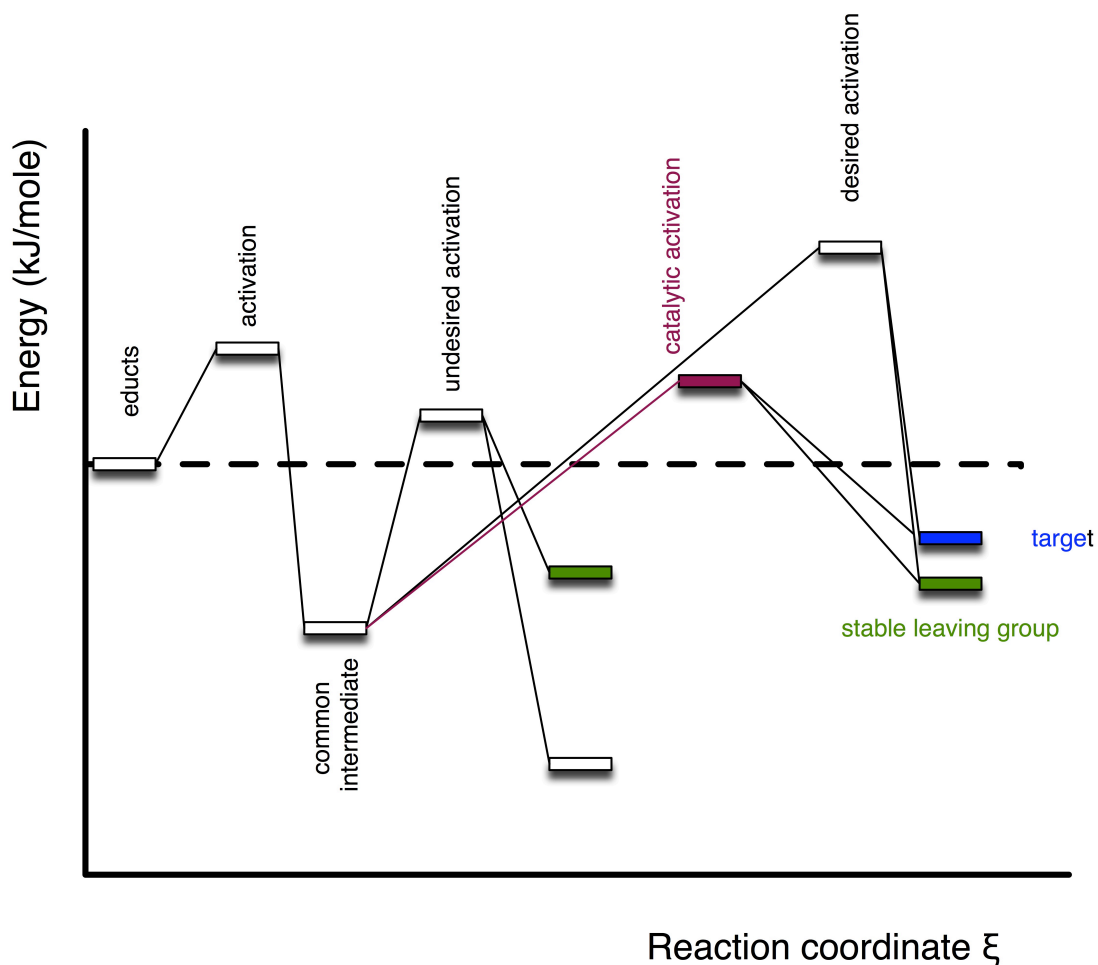
Figure 8: Energy profile of reaction with two product pathways and a common intermediate as primary activation product. Common to both reactions is further the stable leaving group (green). A catalytic pathway (red) to the target product (blue) circumvents the undesired unselective path to the most stable reaction product.

A catalyst is thus a functional material that undergoes cyclic changes in its structure upon interaction with reactants. The design of catalysts thus has two targets:

It must ensure the specific modification of the reactant such that the desired reaction occurs with maximal selectivity and rate.

It must be flexible enough that the structure of the catalyst can undergo reversible changes ensuring that it is not consumed in the desired reaction. This stability criterion is additionally made more difficult as also the reaction products must not strongly bind to the catalyst and thus poison it by irreversible interactions.

A central concept for the structure of catalysts is that of an active site. This active site is an ensemble of atoms guaranteeing the desired geometry of the reactant-catalyst bonding by a highly specific local arrangement of the constituting atoms. In order to ensure the regeneration of the site at the end of the catalytic cycle it is desirable that the active sites are embedded in a stabilizing matrix and that the embedment allows for geometric flexibility in order to minimize the activation energy for the rearrangement of the atoms in the active site.

This is either realized in molecular species where pocket structures of ligands around an ensemble of active atoms enable both specificity and flexibility. In solids special "high energy sites" are terminating a matrix of an active phase providing by its rigid chemical

and geometric structure directing interactions for the reactant binding (such as in pores or at steps of a solid). Examples of both strategies can be found in the chapters on model catalysts and on the biological energy storage systems

A possible catalytic cycle for the process of Figure 8 is shown in Figure 9. A typical reaction would be

$$A_2 + B \rightarrow C + D$$
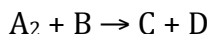
Where C is the target product and D the stable leaving group. For a selective oxidation A_2 would be oxygen, and D would then be water. A possible chemical realization of an active site could be based upon vanadium as the active element. The active site[31, 33] would be

$$[V_2(O_t)_2(O_{br})(O_{sup})_2]_2[O_2]$$
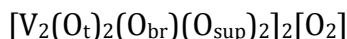
assuming that the active metal changes its oxidation state by one formal unit per catalytic cycle. The various oxygen ligands are O_t: terminal oxygen, O_{br}: bridging, O_{sup}: supporting bridges to the active matrix. It becomes clear that active sites are in general not single atoms or terminating regular entities of active phases. They are rather special structures and often form only during catalytic operation.
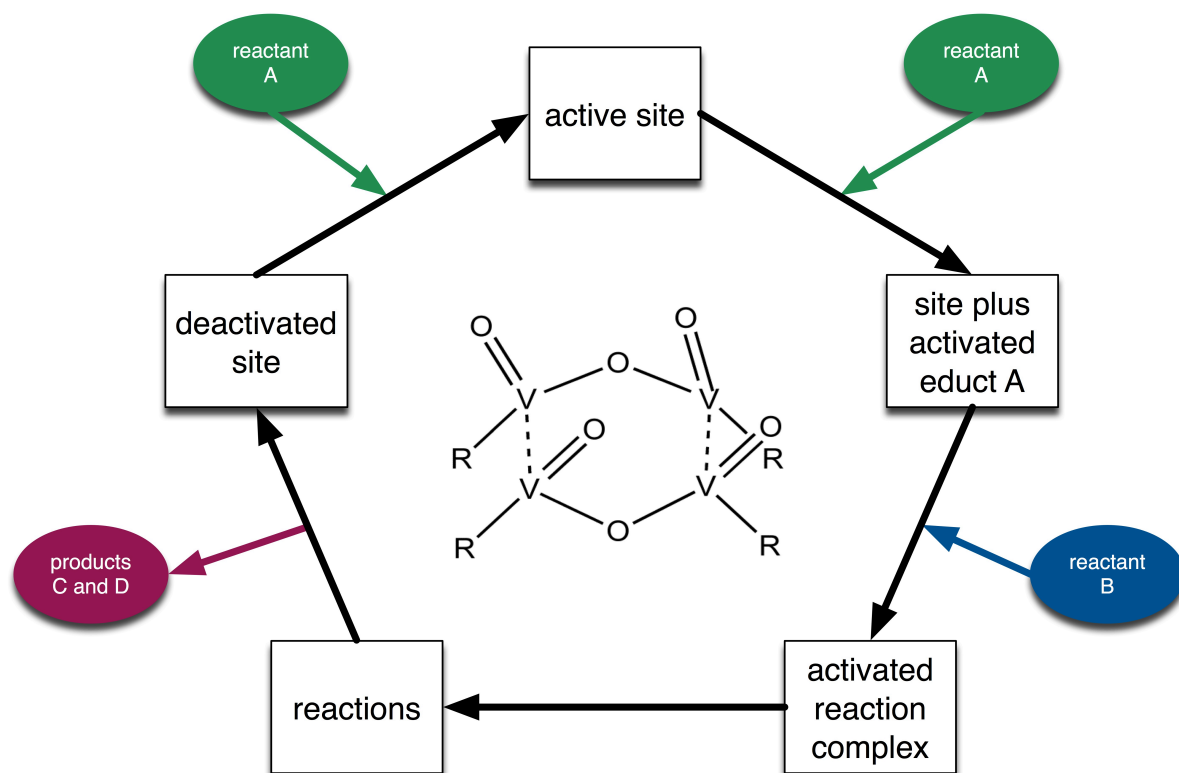
Figure 9. The catalytic cycle illustrates the steps of structural modification of a hypothetical active site represented in the centre.

A schematic representation for the energy-relevant process of methane combustion[34, 35] is given in Figure 10. Here a projection of the energy barriers on a selection of reaction coordinates is shown. The map can be read like a topographic map. The circular structures represent maxima (peaks) in the energy landscape whereas the arrows indicate pathways through saddle points (valleys) of the energy structure. We see immediately that two alternative reaction pathways are possible with one leading through decomposition of formaldehyde to the CO product. The other channel leads via complete dehydrogenation to deep combustion. The dashed lines indicate minor

reaction paths via less deep saddle points. It becomes apparent how the facile combustion reaction is a complex process as soon as elementary steps are considered. It is also clear those catalysts such as Pd or Pt that strongly favor the dehydrogenation path[36, 37] will reduce the selectivity to CO. Finally it is obvious that these catalysts carry the risk for deactivation when the intermediate C atoms polymerize into soot covering the active surface.

Figure 10: Schematic representation of a possible energy surface for methane combustion. The graphical impression is a projection of energy peaks onto a plane of reaction coordinates. The reactant systems (clouds) are not given with stoichiometric accuracy. There are many more intermediates and reaction pathways in the real gas combustion process.
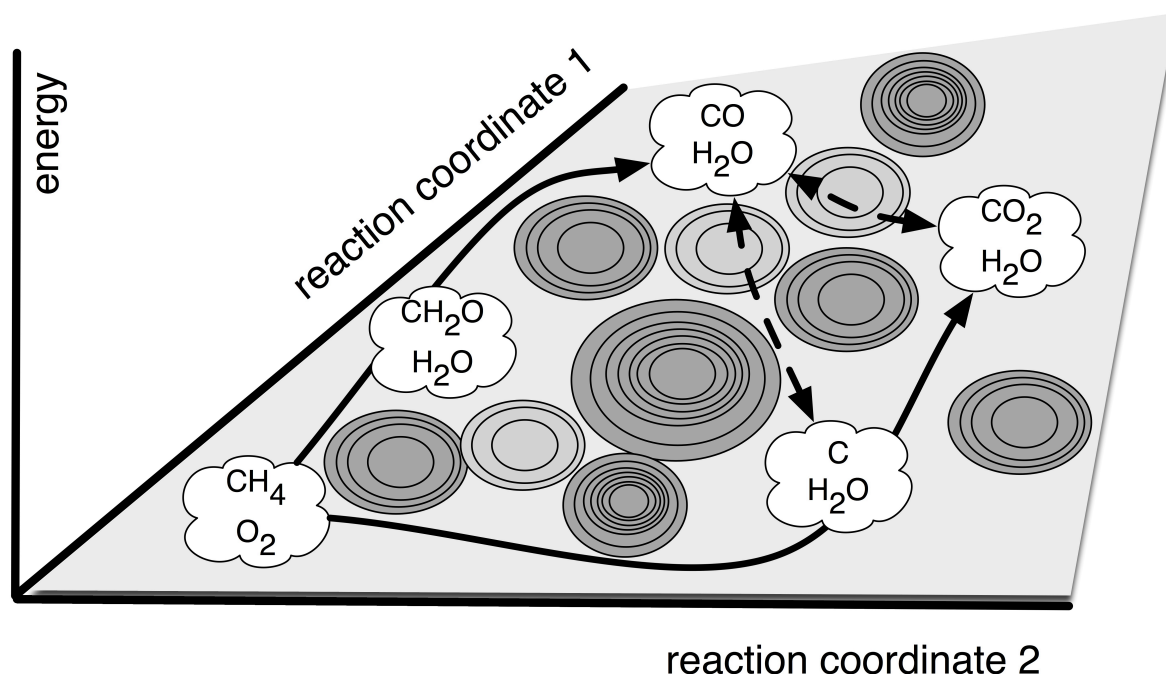
The understanding of catalysis at a level of complexity necessary to analyze the course of a chemical reaction is only achievable through the progress in studying model systems both with experimental[15, 38] and theoretical[39, 40] methods. The model approach was developed with structurally simple single crystal surfaces[41] allowing a comprehensive treatment of elementary step reactions. Most of these reactions were, however, adsorption reactions and only very limited reaction steps such as dissociation reactions were possible. Introducing steps as high-energy sites improved the situation considerably as now reactions such as CO oxidation and ammonia synthesis became amenable to rigorous descriptions. More complex reactions are only recently under study by model systems[42, 43] since a combination of chemical complex oxide support systems with single crystalline quality and their decoration with nanoparticles from metals or oxides became experimentally accessible. In combination with an increasing understanding of the structure of free nanoparticles[44, 45] of active phases it is now possible to accurately describe complex models and study elementary step reactions of kinetically demanding reactions such as alkane activation and C1 chemistry being of relevance in chemical energy conversion processes. Using the well-understood CO oxidation reaction[46] as proxy and probe reaction it becomes increasingly possible to extrapolate structural features from model systems to complex high performance catalysts where the direct structural analysis with the tools of surface science are not

amenable for physical methodical limitations and theoretical models are still of insufficient complexity.

With this knowledge we have now access to elementary reaction sequences of individual molecules. This is unfortunately still insufficient to understand or design performance catalytic processes. The reason lies in the fact that an observable amount of a chemical (energy carrier) contains a very large number of individuals: 1 ml of water contains 10^{22} molecules. One consequence of this large scaling is that the analysis of observable catalytic reaction includes to a large extent effects of transport of molecules and of heat to and from the active sites of the catalyst. These transport effects scale themselves in macroscopic (dimension of reactor) and mesoscopic (dimensions of boundary layers and pore systems) dimensions. Elementary questions such as the comparison of catalysts for their performance "good" vs. "poor" and the determination of kinetic constants and parameters for comparison with model or theoretical predictions and the determination of structure-function correlation[47] by using in-situ analytical techniques all are hampered by the unavoidable incorporation of transport effects. This multi-scale nature of catalysis is reflected in the reaction chain indicated in Figure 11.
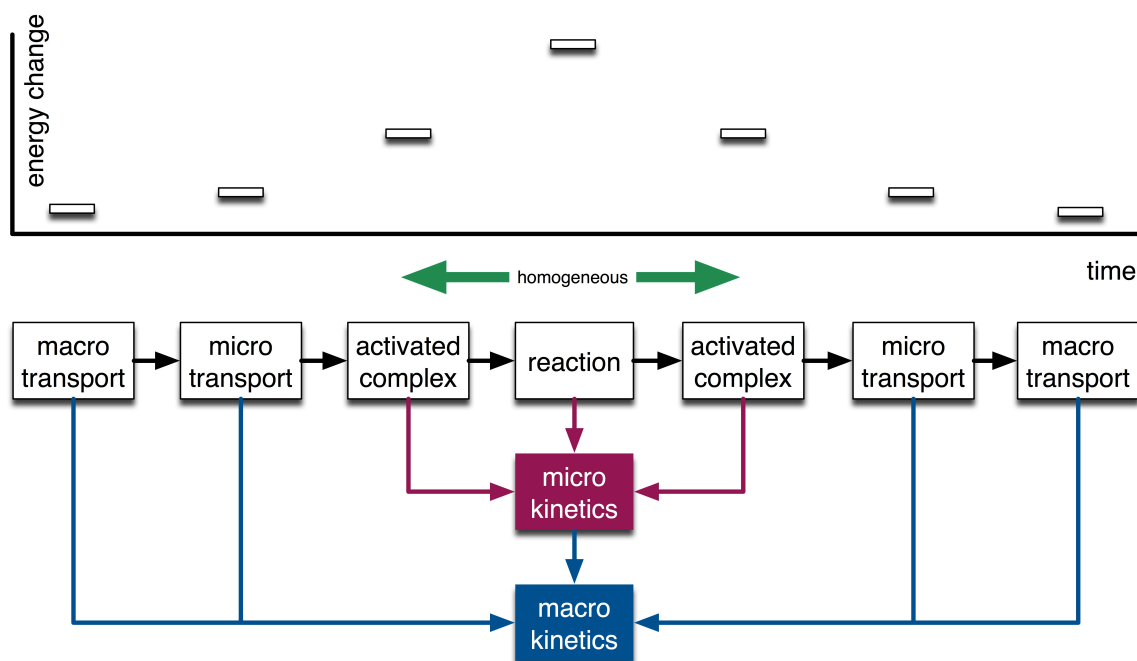
Figure 11: Steps of heterogeneous reactions. The individual processes comprising sequences of elementary step reactions are linked to a process sequence. The microscopic part is described by microkinetics, the observable macroscopic performance by macrokinetics. A typical relative dimension of energy changes associated with the individual steps is indicated. In homogeneous reactions the transport parts are often ignored.

The form of the activated complexes[48, 49] is substantially different in homogeneous and heterogeneous reactions. In homogeneous reaction the catalyst forms a molecular complex between the substrate that is recognized by its molecular shape and the single active site offering a binding site in the form of the replica of the substrate molecule. This is extremely specific in biocatalysts called enzymes and still highly specific in molecular catalysts where a limited set of ligand molecules defines the electronic and geometric constraints of substrate binding. In heterogeneous systems this process is less

specific. Reactants are first chemisorbed on a broad range of surface sites. This interaction is weak with respect to the strength of chemical bonds to be activated. Only in cases of very simple molecules such as H_2 and N_2 the approximations are valid that all adsorption sites are equal on a surface and are not affected by neighboring adsorbed species. The total surface may thus be considered as "landing sites" for reactant molecules. They have to diffuse to special sites where reactions of breaking and making chemical bonds can occur. These high-energy sites[50, 51] are the few active sites discriminating any surface that may adsorb reactant molecules from catalysts that can convert more than once their adsorbates into products. The essentially flat surface location of active sites greatly reduces the specificity that can be executed by the surrounding atoms and chemical selectivity of reaction must be achieved only be exact matching the electronic structure[52] of the reaction site to the molecular electronic structure of the adsorbate. As a result the timing of processes is critical in heterogeneous reactions as a means to induce specificity. This leads to an extreme sensitivity of the catalytic performance to the details of the electronic structure of the solid controlled by many types of defects referred to as "structure sensitivity[53, 54]". A complete description of a catalytic cycle can thus only be achieved by understanding both[55] the microkinetic and macrokinetic aspects of the reaction.

The relative changes of energy with the individual steps in Figure 10 should not lead to the false assumption that steps with small energy changes are less relevant than the chemical reaction bringing about the usually largest energy change. If the molecules cannot access the active sites they cannot perform their role. If the reaction energy cannot be distributed to the environment side reactions can occur and poison the active site or damage can occur for the whole catalyst through the formation of hot spots.

Macrokinetics is the description and analysis of the performance of the functional unit catalyst plus reagents plus reactor. It leads to formal activation barriers called "apparent activation parameter" representing the superposition of several elementary barriers with transport barriers. It further delivers formal reaction orders and rates as function of the process conditions. These data can be modeled with formal mechanisms of varying complexity. In any case these data can well describe the system performance but cannot be used to deduce the reaction mechanism.

This task is left to the micro kinetic modeling[56] trying to observe a catalytic process unfolded from transport limitations. Here sequences of elementary steps are composed in reaction mechanisms with chemically meaningful process steps. These usually complex systems of equations with many unknown parameters are then approximated to performance observations. It is obvious that multiple observations obtained by profile reactor studies and/or by kinetic isotope exchange reactions will greatly enhance the significance of a micro kinetic model adaptation. This approach is presently the state-of-the-art in understanding the relevant energy storage reactions[57].

4. The design of catalysts and processes

The present introduction and the respective chapters of the book may leave the impression that catalysis is a highly complex science and little can be done to systematically identify catalysts. This is a well-supported view as almost all presently

industrially used catalysts were found and optimized by rather empirical methods. The advent of high-throughput experimentation[58] in combination with numerical methods for experimental design has greatly enhanced the empirical testing capacity. It has not led to higher productivities in discovering new catalysts as compared to traditional methods normalized to the same level or resource allocation.

So it may be asked what makes us hope that the enormous challenges of chemical energy conversion being in summary an order of magnitude larger in quantity than our present chemical industry may be based upon effective catalytic processes? The challenge is even larger as the sheer dimension of reactions excludes practically the application of our most powerful catalytic systems namely noble metal systems. Energy catalysis must after all be sustainable and scalable[59]. It must not occur that energy-related processes require more functional materials than globally available (economic and societal problems) nor must it be that energy-related reactions create waste and non-useable byproducts. We are thus limited in process design to systems that only leave uncritical wastes such as oxygen, nitrogen and water, we must close all material loops of species with critical biological effect such as carbon, nitrogen oxides, ammonia and we should render our process materials fit for recycling mineral resources such as metals. These boundary conditions limit the parameter space for designing catalysts enormously.

This is true to an extent that is worthwhile to ask if fundamentally we will be able to address all these demands. We need conceptual technologies mapping out parameters spaces with so many boundary conditions. A most suitable theoretical approach[60] to this problem is the method of scaling relations. As basis an in-depth theoretical model of the reaction of interest is set up delivering critical parameters of adsorption and reaction. These critical data are than calculated for a large number of elements and surface geometries ignoring all details of the chemical reaction. As it turns out that many reactions are controlled by a small number of critical properties[61] of reactants and surfaces, a database can be built allowing correlating hypothetical performances to fundamental properties of elements and compounds. This scaling can also include non-chemical variables such as the prize of the constituting elements and one can predict the catalytic performance of a reaction against the prize of the catalyst used. From such predictions one may conclude that it is not impossible to find chemical solutions for energy conversion reactions that fulfill all boundary conditions of scalability and sustainability.

One reason why the problem is not solved yet lies in the complex challenge of making and stabilizing the required functional materials[62-64]. Here aging homogenous and heterogeneous catalysis is widely different in its development and maturity. The respective chapters of the book give insight into the state of affairs as well as into critical research desiderate that need to be addressed to advance in this most important subfield[65] of chemical energy conversion.

Despite this limitation the progress that catalysis science has made over the last 5 decades allows foreseeing that it will be possible to systematically design[48, 66, 67] catalysts for energy applications that are not built upon the past empirical practice "intuitive knowledge". The new systems will be built upon design criteria arising from the set of boundary conditions for energy processes. They will further use the insight into structure-function relations that are now accessible both from functional models

and from high performance but unsustainable existing catalytic systems (such as systems based upon noble metals). The recently developed suite of in-situ functional analysis[68] of working catalysts and the progress in atomically solving structures[69-71] of enormous complexity[72] are the tools that were not available in earlier phases of catalysts evolution. Also the conceptual understanding of catalysts as dynamical systems with few differentiations between homogeneous and heterogeneous systems is a new asset to the catalysis scientist. The strong pressure from chemical energy conversion upon the catalysis science and technology will help advancing the academically available strategies and analytical technologies into a broad-based catalyst development effort conducted in collaboration between industry and academia. The history of chemical industry has seen such periods of highly fruitful and easy technology transferring periods before and after the wars in the 20th century. It may well be that we at the onset of another such phase of revolutionary development. It is understood that evolutionary strategies and incremental developments will not be sufficient to respond to the challenge of chemical energy conversion and storage.

5. The biological origin of our present energy system

Our present energy system is largely built upon fossil energy carriers dominated globally by oil. These energy carriers are hydrocarbon molecules with a largely varying hydrogen content between C:H = 4 for methane and C:H = 0.1 for coal variants. These hydrocarbons stem from biomass that was converted in several steps from oxygen rich structures typically $C_6H_{12}O_6$ to polymers (humic acid) and then by de-oxygenation to hydrocarbons. In cellulosic biomass the lignin content is already much closer to the condensed structure of coal leading to the fact that lignin from ancient trees was a predominant precursor to coal.

All fossil materials were initially generated through photosynthesis[73] leading to glucose as primary source of biomass. The photosynthesis process using water as reductant and thus liberating di-oxygen as waste is the largest chemical process on out planet creating all life, all food and all energy carriers from sunlight. Its homogeneous catalytic reactions are described in detail in a chapter of the book as they are of prototypical character for energy storage processes. It is noted that this process operates isothermally and is highly endothermic:

$$6CO_2 + 6\ H_2O \rightarrow C_6H_{12}O_6 + 6\ O_2$$
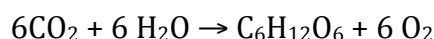
$$\Delta G` +2792\ kJ/mol = \Delta H\ (2813\ kJ/mol) - T\Delta S\ (293\ K \times 182\ J/mol)$$

180 g of sugar (glucose) are well sufficient to nourish one person for one day. It is evident that nature uses a dense form of energy storage. The free energy $\Delta G`$ is related to biological conditions of 293 K and pH 7 in water. The two molecules water and CO_2 are thus the key elementary ingredients into the energy system of life that requires several other critical inorganic ingredients in trace amounts to build the molecular systems catalyzing the conversion of sunlight into the storage molecules. A systemic relation between relevant processes is given in Figure 12.
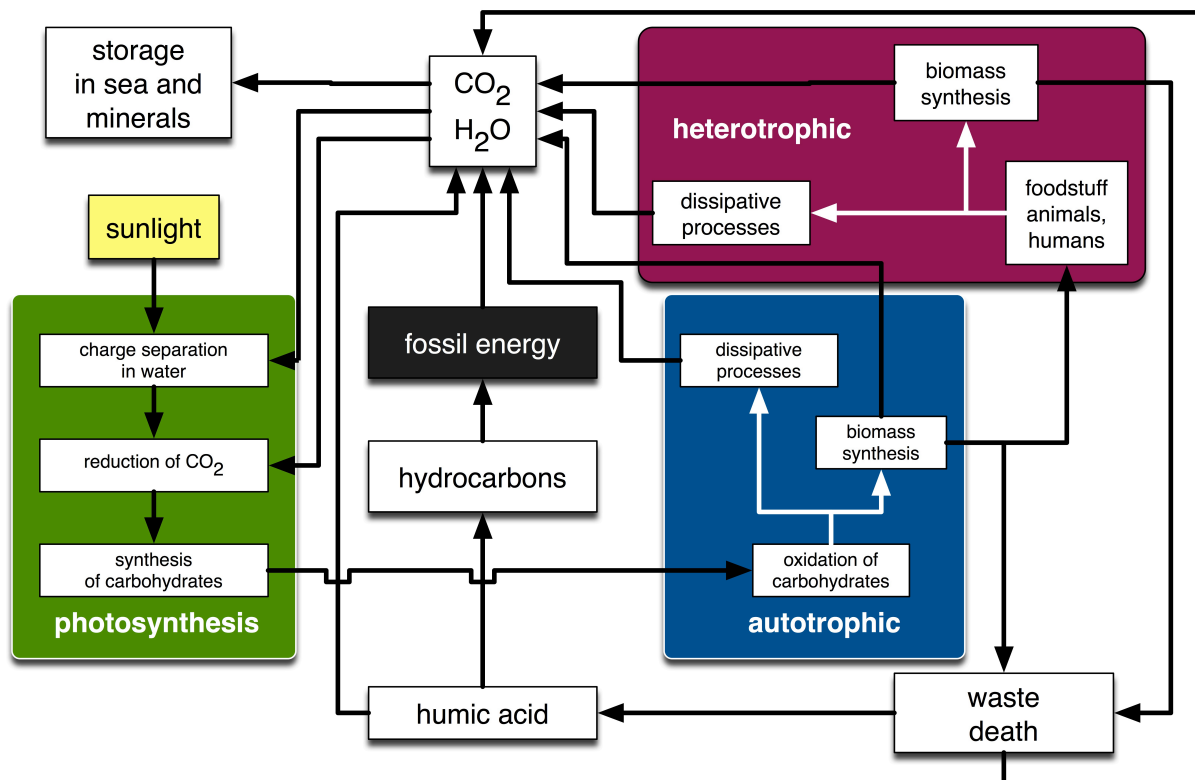
Figure 12: A crude systemic picture of the biogeochemical processes from which fossil fuels derive as non-oxidized storage system of nature.

The dimensions of the material and energy flow are enormous on dimensions of our planet. The table taken from the IPCC report gives some crude estimates.

Geosphere compartment	Stored carbon in Gt	Exchanged carbon in Gt/a
Deep sea	13800	
Surface sea	1020	
Sea-atmosphere		92
Fossil energy carriers	4000	
Combustion to atmosphere		5.5
Atmosphere	750	
Vegetation	610	
Photosynthesis		121
Soil	1580	

These data underline the enormous dimension of photosynthesis and the biosphere for energy conversion. From these figures it could appear that there is no need for any artificial chemical energy conversion as there is abundant natural energy conversion. Mankind only burns 4.5% of the annual photosynthesis fixation of carbon. If we convert this into annual electrical energy equivalents we arrive for photosynthesis at about 250 TW and for total human consumption at about 15 TW. In this argument we first have to add the electrical equivalent of our food energy that is and has to be produced by photosynthetic processes and related food chains. This energy amounts to about 25 TW. If we add our demands for cellulosic biomass as feedstock (wood, pulp) and consider that about 65% of the biomass production on our planet occurs in the surface-near sea but our demands for food and feedstock is largely related to land-based organisms then

we seen that the calculation gets tighter. If we add the most critical but difficult-to-assess factor of ecosystem stability allowing only a fraction (about 30% without sustained damage, see fish and grasslands for example) of any ecosystem to be managed by man then we see quickly that we cannot rely by enlarge on biological processes for converting energy from the sun in useable energy carriers for technologies. In this estimation we have further to consider that the global population is fast growing, which requires first more food and then technical energy carriers.

Another issue is the required energy density. One metric ton coal as 1 t SKE contains 7,000,000 kcal. 1 ton of dry glucose contains 3,720,000 kcal. Biomass does not occur as dry glucose but rather as diluted and/or polymeric forms of glucose. Several steps of energy-intensive concentration and refining are required until we obtain glucose for technical applications. The relevant chapter in the book discusses potentials and difficulties of this often overlooked aspect. That is also true for the many concepts of using algae or other aqua-plants requiring harvesting drying and refining before it can be used as energy carrier material.

The apparent initial success of biomass derived energy carriers used in biofuels[1, 10] and fuel additives (E10) stems from a non-sustainable form of biomass harvesting. These materials are generated from the fruit of plants. These fruits are developed to carry a high-energy biomass such as starch or oil in order to support the reproduction of the plant. In fact, only a small fraction of the total biomass of the plant is concentrated in the fruits. In addition, the extensive bio-catalytic processes of biomass formation for these fruits (see Figure 12) is highly energy-intensive for the plant: a large fraction of the effectively harvested solar energy is thus "wasted" in the biological processes generating the fruits for generating biofuels (of the first generation). This form of energy farming is suitable as niche solution in areas where an excessive abundance of arable land is available in relation to the needs of the regional population. As a global solution it is inappropriate also due to many non-scientific consequences of energy farming (see also Figure 4).

Large-scale application of energy farming further raises the question about sustainability of land use, water use and availability of mineral fertilizer components such as phosphate and soluble nitrogen. It is foreseeable that competitive situations of these limiting resources on the planet may occur against food production. Even if we solve the land use issue by appropriate land management (not yet practiced) the other resources may prevent the use of energy farming as a main source of renewable energy generation.

Whatever biomass may be spared from either keeping the ecosystems stable or from feeding the global population, it may be used as feedstock for chemical processing rather than as fuel for combustion processes. In this way the complex structures nature has generated during biomass formation (see Figure 12) can be partly preserved and may be brought to use in material applications such as polymer formation or direct synthesis of intermediates with complex molecular structures. In order to follow this highly constructive use of biomass it is essential to understand the underlying chemistry of biomass transformation[74-76] being largely different from our well-studied hydrocarbon transformation. In the later case we need to enhance the functionality of hydrocarbon structures (gas and oil) whereas in biomass transformations we need to

de-functionalize over-functionalized molecules leading upon activation to poly-condensation processes with unwanted poly-oxo structures (such as humic acid).

An in-depth analysis of the potential of biomass to sustainably cure the CO_2 emission problem arising from burning the fossil resources (see Figure 12) revealed that this is no permanent measure as compared to reducing the irreversible emission of CO_2 from fossil sources. "Although terrestrial ecosystems can be managed to reduce carbon emissions and increase carbon sink size significantly, such increased carbon uptake can offset fossil fuel emissions only temporarily—on a time scale from decades to a century. Terrestrial carbon sinks are thus best viewed as buying valuable time to address the most significant anthropogenic perturbation of the carbon cycle—fossil fuel emissions.[77]"

6. Chemical energy storage: one long-term solution

It is now obvious that we have to refrain from irreversible CO_2 emission as fast as we possibly can. All classes of influences indicated in Figure 4 point in this direction[1, 78, 79]. This is a long-term trend and not a shorthand political wave. As the dimension of this challenge is so large we are advised best if we use all options that fulfill the conditions of scalability and sustainability in order not to create a new energy system with a similar flaw in it as our present fossil system. In this sense chemical energy storage is one important option but certainly not the only solution.

On these grounds it is foreseeable that solar energy with enormous but rather dilute energy flux onto our planet will be a central source of future energy. Besides the dilute form ($200W/m^2$) the volatility of its flux at ground is the main obstacle. It is impossible to sustain uninterrupted energy flux at demand if we use solar energy directly converted into primary electricity. This approach is despite its volatility highly efficient, as we need about 50% of our primary energy carriers for generating electricity. If this comes without a CO_2 bill and without cost for fossil fuel it would greatly relief the energy system. It is also quite efficient: In Germany 1ha land with solar panels generates about 1,000,000 kWh/a electricity. Would the same land be planted with corn, then the energy equivalent from biomass to biogas conversion plus conversion into electricity at demand would generate 15,000 kWh/a. Would this field host a wind turbine in addition then an additional solar power of 2,085,000kWh could be added. If we assume that such a "combi-energy-field" could generate 3 GWh/a ha then in Germany an area of about 2000km^2 could generate all electrical power consumed in Germany. This is all possible with existing technology. The investment would be substantial[80, 81] with about 2.000€/kW for solar and about half as much for wind and biogas but as solar energy is free and thus low operation cost would partly compensate for this investment that is crudely estimated twice as high as the investment in conventional fossil power stations with a mix of coal and gas.

The remaining fundamental problem is the volatility. Even when solar power and wind power are combined and exchanged over the area of central Europe this would not be sufficient to guarantee the uninterrupted supply. Solar power has in Europe a pronounced annual fluctuation[82] and wind is quite unpredictable onshore and still not always available off shore.
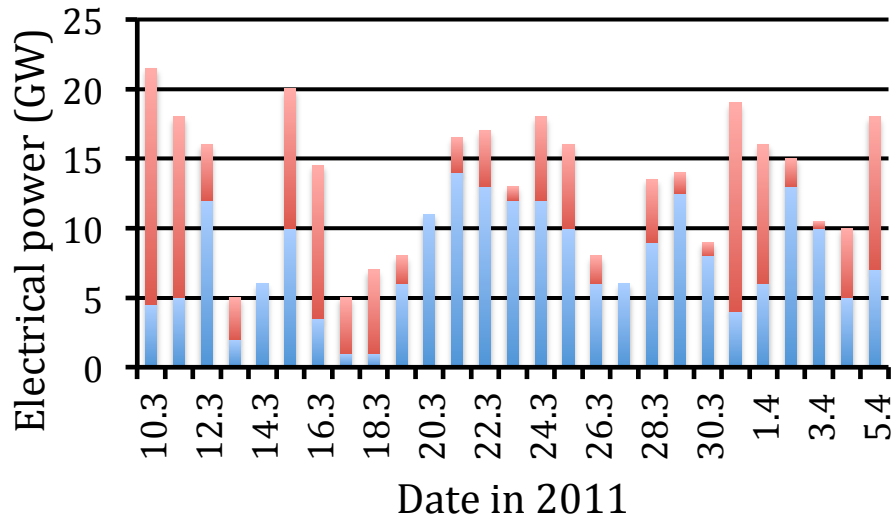
Figure 13: Regenerative power in Germany from wind (blue) and photovoltaics (red). This episode accounts in its maxima for about 25% of the electricity demand. Source: data from bdew.
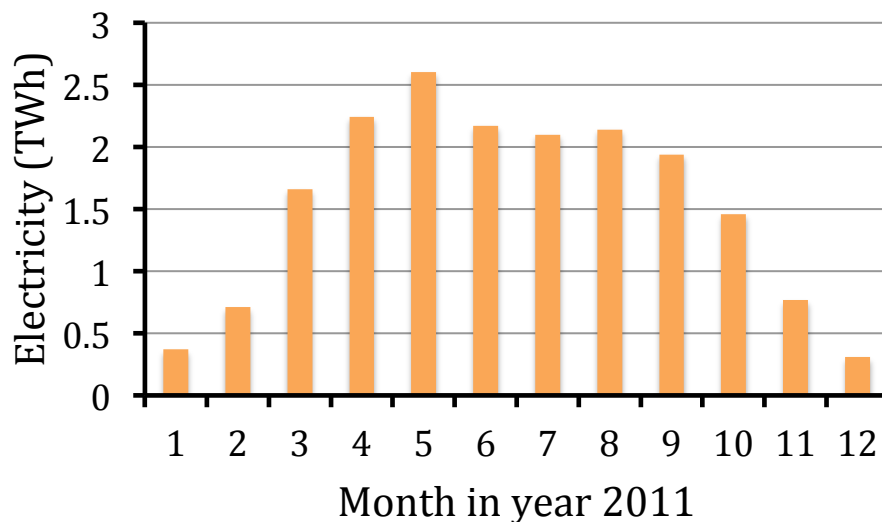
Figure 14: Annual change of PV electricity production in Germany for the year 2011. These data change somewhat with the weather over the years. Source: data from BSW solar.

These trends are indicated with data from the German electricity production in Figures 13 and 14. The total contribution of regenerative power to the German energy system was about 16% in 2011 including, however, a significant fraction of thermal energy from waste incineration. In Figure 13 an episode in the spring season is shown with its contributions from wind and PV electricity. Comparing to an average total demand of about 70 GW, we see that on certain days the contribution of regenerative power is already significant. There are also periods with no sunshine and no wind where little contribution comes from regenerative sources. In many instances it is fortunate to combine PV with wind power to equalize the volatility. A critical problem is the gradient of change being very fast on the timescale of compensating measures with fossil power plants. Here import/export helps but quantitatively larger fluctuations would tend to destabilize the whole energy system. This issue gets worse when the temporal resolution is increased: PV power has a strong day-night cycle that is predictable

whereas wind power is completely unpredictable in shorter timescales. These fluctuation cause challenges for management of grid, power stations and possibly the demand situation. It limits the amount of renewable power that can be tolerated in the grid with its present structure.

The issue of volatility has also a dimension on much longer timescales than days. This is shown in Figure 14 for PV data of 2011 in Germany. A strong winter-summer trend is clearly visible stretching over almost one order of magnitude of power change. This needs equilibration with storage measures that can hold energy in large amounts (production of the total solar installations) for several months. It is noted that the electricity production of PV in Germany now already exceeds the storage capacity of the national hydro power stations.

The data clearly reveal that future energy systems relying to a large fraction on regenerative primary energy will need substantial capacities for energy storage. These storage systems need different response times from minutes to months and are thus combinations of physical (short-term) and chemical (long term) storage solutions. It is also clear that an intelligent management structure of the energy system is needed deciding which storage option is used at what demand/supply ratio. The sheer amount of energy that needs to be stored certainly cerates strong boundary conditions on economics, efficiency and scalability of the solution.

The data in figure 13 indicate what kind of temporal structure is needed for the chemical processes storing energy. Energy conversion systems such as electrolysis need response times of several hours between full load and low load. As dimensionally stable electrodes are still a great challenge[82] it is a combination of distributed systems switched in cascades and an operation scheme leaving partial load on the electrodes for a maximum time that may solve the challenge. This random example illustrates the complex requirements for energy storage systems many of which are at present not met with proven reliability causing research needs both with applied systems and on the fundamental level to understand the adverse effects of load fluctuations.

In general will the substantial contribution of volatile power sources change the operation scheme of the whole energy system as the traditional distribution in continuous base load and discontinuous peak load does not apply. All elements of the energy system will need faster response times creating not only issues for the economic operation of large scale installations and transmission capacities but also creating new demands on structural und functional materials having to cope with frequent changes of operational loads.

The solution of these issues will benefit from the availability of large-scale chemical storage of electrical energy[18, 83] in artificial solar fuels that can counteract the volatility of primary electricity in central and distributed installations. This has, however, a price tag[11, 13, 80, 84] arising from complexity and new optimization criteria. In Figure 15 a crude schematics of the present energy system in Germany is shown to illustrate the existing key components.
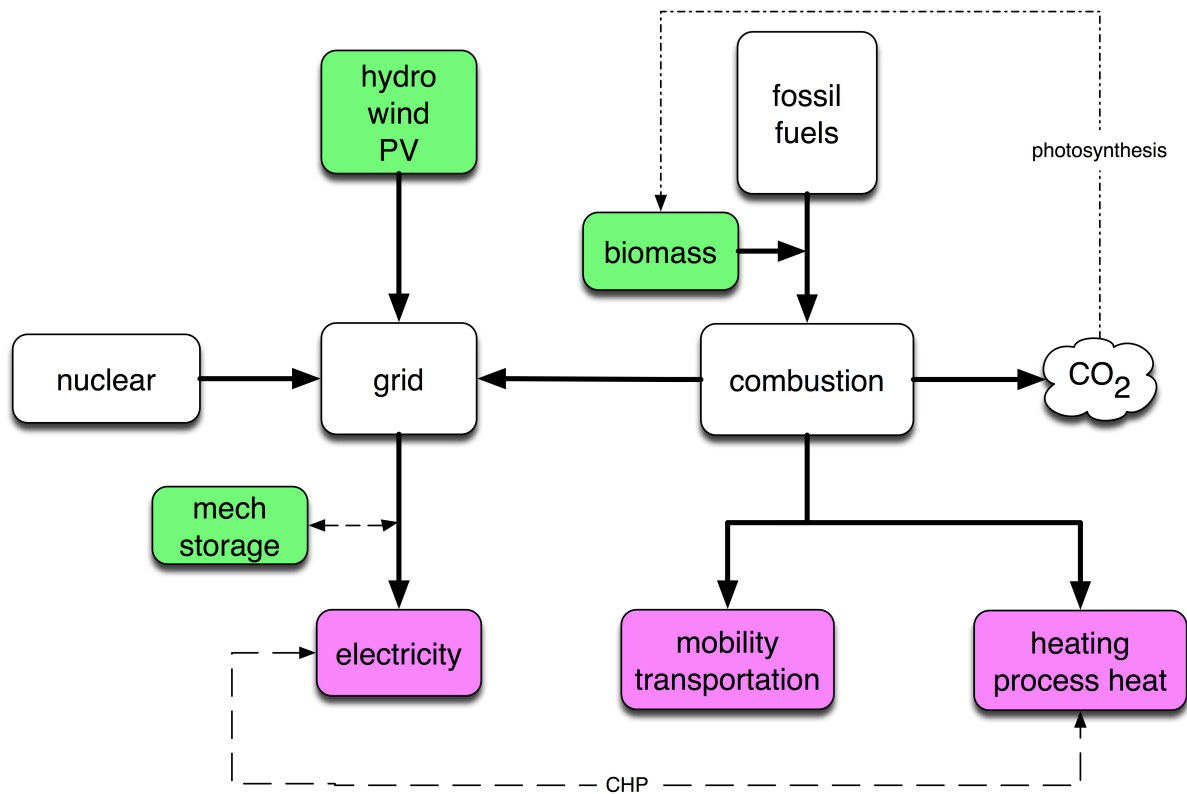
Figure 15: Schematic representation of the German (European) energy system.

By enlarge we generate our free energy from combustion of fossil fuels with largely irreversible CO_2 emission. The existing grid manages fossil electricity with nuclear electricity in a common system and guarantees the uninterrupted supply according to demand. Some mechanical storage in pump hydroelectric stations, export/import across national borders and increasing use of CHP systems help stabilizing the power distribution and efficiency. The contribution from renewable sources is substantial with about 16% of the grid demand and reaches its limit due to volatility problems in the present system.

This system is optimized with respect to electricity according to traditional large-scale consumers in locations of power stations and transmission lines. It is not suitable for a national distributed power generation from renewable sources and from the exchange of large amounts of renewable energy to locations where massive nuclear power installations exist. It is further optimized to use economical primary energy carriers such as coal and lignite and uses gas power stations for meeting fluctuating demands. The overall optimization criteria were prize of electricity and a maximum availability of the grid service.

The criteria and targets for optimization infrastructure[6, 11] and services require modifications when as new boundary conditions the abandonment of nuclear power and the minimization of CO_2 emission are brought into place. According to interconnections illustrated in Figure 4 it is first essential that all stakeholders agree on these new conditions. If we retain the condition of maximum availability of service then it becomes quite clear that new architectures are needed. This in turn will cause massive investments and incentives for industry to install new technologies. Some of them do exist and need rollout such as primary electricity generation, mechanical energy storage and a smart grid, some others need to be created. This is a long process and will also

need financial investments as well novel industrial structures. The total cost of such a system transition is hard to estimate as against the new cost also savings for purchasing primary energy carriers, saving of cost for socialized risks of resource availability and mitigation of climate change and cost for maintenance of the existing infrastructure will be reduced. Such assessments and model development is clearly not the task of scientific discourse but scientific results will be needed in these assessments in order to come up with reliable estimates of requirements and cost.

In return, the priorization of research in terms of cost expectations of a target technology is quite a limitation that needs to be conducted with great care. The technological revolutions of the past document impressively (imagine the cost for cellular telephones and data transmission or the cost of the internet and their business cases) the unpredictability of scientific progress. Energy science should thus concentrate on creating options for solutions including all the data required for reliable life cycle analysis and cost estimates and then inject this information in societal processes taking decisions. As such societal processes control science funding, a non-negligible feedback exists between the two spheres, which requires science to be aware of the interfaces shown in Figure 4. A particular difficulty with this feedback loop is the inherent volatility of societal processes being much faster that the timescales needed for fundamental and applied science breakthroughs. The history of biofuels with its premature decisions and resulting detrimental consequences for science and society is a vivid exemplification of this extra hurdle in energy science.

In any case a working hypothesis for energy systems should exist into which new scientific inventions and achievements in fundamental understanding can be brought in. A special responsibility for the reliability of scientific activity arises from the lifetime of energy infrastructure of several human generations calling for careful plausibility checks. They too benefit from such a working hypotheses, in particular when it comes to long-term fundamental efforts and its assessment with respect to usefulness of the targets. Such a working hypothesis for the electricity generation is shown in Figure 16.
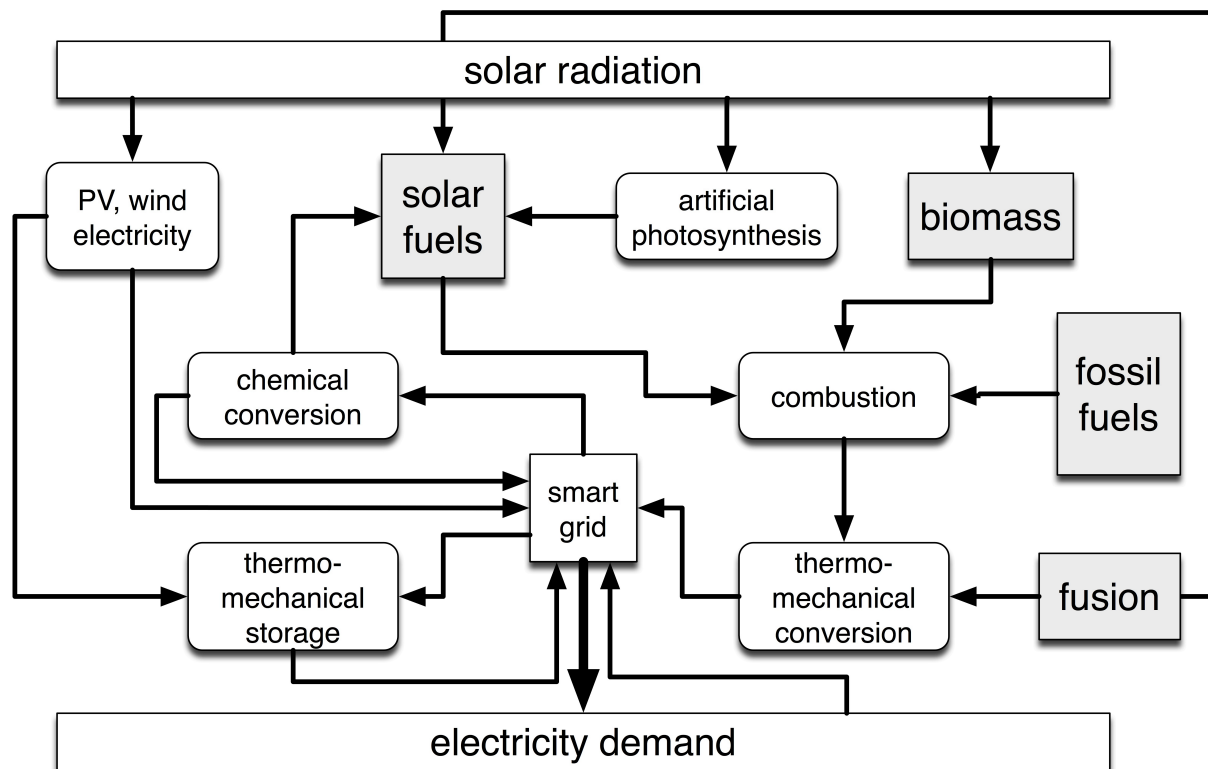
Figure 16: A possible structure of the electricity part of a future energy system.

Multiple feedback loops and a central intelligent distribution system managing the generation and storage of electricity characterize the system. It uses further several energy carrier systems including the present fossil fuels to allow gradual adaptation. It assumes the existence of several storage systems accommodating the varying requests for storage times and storage amounts. Both physical storage (existing) and chemical storage (in development) are assumed to be operative. The system also assumes feedback between energy demand and generation allowing non-critical or prize-conscious applications to be controlled in their time structure. This has, as far as non consume applications are concerned (are they worth the investments if they are served in a energy-efficient way?) the consequence that also large-scale electricity users may restructure their processes to accommodate temporal fluctuations. A core consequence will be that the traditional structure in base and peak load may vanish both from the supply and the demand sides. This is however, a medium-to-long term process.

The structure of such an energy system is substantially more complex that the existing system. Besides the economic consequences it is essential that the central and strategic management capability of such a system is much better developed than at present. This requires substantial evolution of science and technology of informatics. The fossil fuel component is bound such into the process chain that it can phase out gradually. The velocity of this process is controlled by non-technical boundaries but also the progress of understanding and implementing the multiple new technologies standing behind the superficially simple feedback processes assumed in the diagram will limit the speed at which we can refrain from further irreversible CO_2 emission.

The process "chemical conversion" in Figure 16 is of central importance in the overall scheme. It ensures the storage of electrical energy in chemical bonds. For this task principally the operation of accumulators "batteries" and the formation of material

energy carrier are possible solution. The concept of a redox-flow battery[85] is a hybrid between the two concepts. Battery science[86] is a crucial component although it is evident that grid amounts of electricity will not be stored in batteries. Their fast temporal response, their all-electric control process and their ability to operate easily in distributed or mobile systems are however attractive properties. Their potential in e-mobility applications is a further attraction. This application is not large with respect to the total energy system but it covers an important functional aspect the satisfaction of mobility demands in urban areas where a good fraction of the total global population lives. Although the fundamentals of battery applications are already well understood[87] their implementation in sustainable technologies and materials is still in its infancy. Here we see that largely empirical science that dominates the present efforts can lead to impressive initial success but the exploitation of the full potential of batteries will need a much deeper fundamental-grounded effort that is still missing. A similar situation we can state in electrolysis[88]: this traditional technology is still in its infancy despite market requests as both the understanding of the process under high-performing conditions and the respective material science are insufficiently evolved. Considering that natural as well artificial photosynthesis[89] work on the same scientific concept of electrochemical water splitting, it is of high priority[67] to advance our full understanding of water splitting in the context of both heterogeneous and homogeneous electro-catalytic processes.

For chemistry the central target besides enabling energy-saving strategies is to generate options and technologies for chemical energy conversion of electricity, for converting the resulting primary energy carrier hydrogen into solar fuels and for back-converting these fuels in energy efficient ways into electricity. In addition the enormous task to develop artificial photosynthesis needs still massive fundamental research efforts. The possible improvement of exploitation of natural photosynthetic energy conversion strategies both at the level of modifying living structures and at the processing of the resulting biomass is another area of fundamental as well as applied research for chemistry. It is obvious that all disciplines of chemistry are involved in this challenge. The timelines for solving these challenges is decades rather than years. This does, however, not imply that in selected areas where we can build on longstanding research efforts rapid breakthroughs and emerging technologies may occur within the first decade of concentrated and interdisciplinary research that is about to come into operation at the time when this account is being prepared.

At a more detailed level a core involvement of chemistry into energy science is the generation of knowledge and technologies allowing operating a solar refinery. Such a hypothetical plant schematically shown in Figure 17 converts primary electricity and solar heat into hydrogen. Together with a feedstock of CO_2 from biological or fossil sources it generates fuels of identical or similar chemical structure than present-day fuels. These fuels can use existing distribution and storage systems (gas pipelines and underground reservoirs for example) and can be converted to free energy in existing applications (cars, power stations).

Figure 17: The solar refinery as the conceptual contribution of chemistry by chemical energy conversion to the sustainable use of renewable energy. The upstream part (hydrogen generation) and the downstream parts need not to be co-localized in a practical realization. Green boxes indicate solar fuel products; blue boxes stand for intermediate platform chemicals. The red arrows indicate flows of solar hydrogen to a storage and transport system for large-scale applications. The red arrows show the major application lines for chemical production of solar fuels. The scheme also indicates the role of fertilizers from ammonia required in sustained use of biomass for energetic applications.

The carbon cycle must be closed. This can be done by using biomass as source of CO_2 or for stationary sources such as gas power stations by collecting the CO_2 from combustion of solar fuels in the same way as for fossil fuels (carbon capture and use CCU). The emissions from distributed sources can only in limited dimensions be collected by biomass as argued in the previous text and in the respective chapters of the book. Using other storage options such as batteries or thermo-mechanical solutions for small stationary applications should reduce CO_2 emissions. The energy system can alternatively omit the use of carbon-based solar fuels by either working on hydrogen when it is also generated in distributed systems or by using ammonia[90, 91] as a non-carbon based energy carrier. It is expected that all these options will be realized, in particular when we consider energy systems for other parts of the world than Central Europe.

 A large variety of options indicated in the upstream hydrogen generation section reveals that much room exists for innovative chemical approaches for water splitting. It must be clear however, that the predominant part of these reactions must split water under liberation of di-oxygen or chemically speaking by using reducing equivalents from oxo-anions. We are not interested in the oxygen molecule representing like in photosynthesis a "waste" but we need the electrons carried by to oxo-anions.

$$2 H_2O \rightarrow 2 OH^- + 2 H^+ + 2e^-$$
$$2 OH^- \rightarrow O_2 + 2H^+ + 2e^-$$

Many creative solutions circumventing this most difficult elementary step in hydrogen production can only be niche solutions as long as they work on sustainable other sources of electrons from e.g. biomass debris. Many intelligent physico-chemical approaches that use stoichiometric electron sources from non-renewable sources are not suitable solutions. If we plan to use other sources of electrons such as reduced metal oxides then we must make sure by lifecycle analysis that such options are competitive with straight electrolysis including the use of material and the efficiency losses through the need to operate at high temperature levels. Many challenges of hydrogen generation would be relieved if we had available a source of non-solar but sustainable high temperature. This is indicated in Figure 16 with the use of fusion power helping generating hydrogen from gas phase electrochemistry and using the resulting intermediate temperature of a heat carrier for conventional thermo-mechanical power generation. Photochemical water splitting[92-94] with oxide or nitride photo-electrodes is a wide field of chemical research. It qualifies as artificial photosynthesis[95-98] in the scheme of Figure 16 even when "only" free hydrogen would result. Despite enormous progress there is still much to do from the basic understanding of coupling electronic excitation with catalytic surface chemistry to reproducible and scalable production of photoactive materials and suitable reactors allowing separating hydrogen and oxygen gas products.

On the downstream side the development of effective catalysts is the core challenge. These systems should avoid noble metals and should allow process operations resulting in a minimum of byproduct formation in order to minimize separation and purification steps for both the intermediates and the final products. In particular, at the level of final products the admixture of trace impurities absent in present-day fossil energy carriers can cause enormous barriers of application. A random example is the admixture of traces of hydrogen in solar gas or wind gas sources: its presence would cause hydrogen embrittlement in the medium-to-high pressure part of the pipeline and pumping systems and thus upset the whole existing infrastructure. Taking this into consideration and remembering the likely need to operate energy conversion processes in decentralized small scale units and at varying process conditions of partial load illustrates quickly that we are far from having robust solutions even for process steps that are conducted in present chemical plants such as ammonia synthesis or Fischer-Tropsch processes. The boundary conditions come from system requirements upstream and from the components of the energy system shown in figure 16 and must be met by the chemical process steps. We can expect that such an approach will take time to be built into future chemical process and catalyst development efforts.

The question is critical about the time structure of changes in energy systems. From the point of climate protection we need to stop growing the CO_2 emission immediately if we want to limit the climate change consequences to a "manageable extent". The German Energiewende has a milestone in 2021 with the end of nuclear power plants. Many technologies for energy conversion from primary electricity are in their infancy. Artificial photosynthesis is yet a projection. The most pressing inputs stem from the availability of fossil resources. No pressure comes from coal and gas in the next decades as large resources and still large reserves exist. A critical driver for a change in energy systems may come from oil. At the time of preparation of this text we are about at "peak oil"[16], at the maximum of oil production that will from now on decline as no more new

reserves are being found and the easily accessible reservoirs are becoming depleted. This trend is seen in the data of Figure 18. The decline in production is smoother than expected as the contribution of difficult-to produce reservoirs is increasing with the inevitably increasing prize. Even with large uncertainties about the future[16] it is clear the enormous demand of the past 50 years led to a rapid exhaustion of the easily available oil resources. It may thus be expected that for oil-critical applications such as mobility technologies (airplanes, trucks, passenger cars) or chemical industry feedstock the request for renewable sources of solar fuels may come faster than expected from the modification of the electricity system discussed with Figure 16. Without knowing the fastest driver for changes in the energy system it is likely that in the coming decade severe pressures on the existing energy system will increase the pressure for new energy sources. The chemical energy conversion strategies will here play strategic roles. It is apparent from the texts of this book that we have some solutions in place and prepare for several breakthroughs in underlying science such as in understanding of photosynthesis or in catalysis. But it is also clear e.g. from Figure 19 that we far apart from being able to replace fossil sources at the dimensions that they are consumed at present.
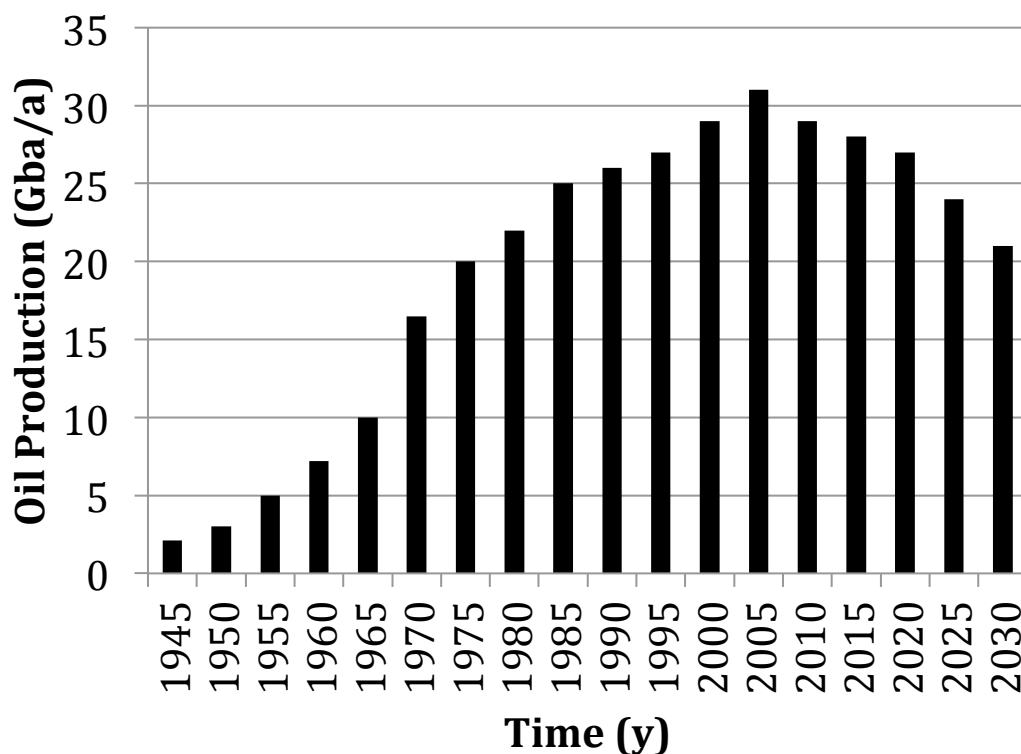

Figure 18: Peak oil. The graphics shows on a crude timescale the temporal evolution of oil production. The low resolution was chosen to identify the main trend irrespective of multiple events in shorter timescales such as the oil crisis. 1 Gba is 1.56×10^{11} l crude oil. Source: data from www.peakoil.com

In conclusion, the present chapter gives a crude overview of what it takes from the side of chemical science to engage into the energy challenge. Future energy systems will be based substantially on renewable solar primary energy but cannot be operated without a suite of technologies of chemical energy conversion dealing with storage and inter-conversion of energy carriers. The strategic and central science in this endeavor is catalysis much in the same way as it now enables the operation of chemical and petrochemical industries. The insight and progress in understanding this physico-

chemical phenomenon allows predicting that the challenge will be met at a level higher than that enabling the evolution of the present energy industry. Despite promising activities a still enormous scientific, technological and economic effort is needed to initiate the turn of the energy system apart from the dominance of fossil energy carriers. The technologies of physical energy conversion by PV and wind and other innovative concepts are far ahead of the chemical technologies. The combined efforts of science can be made faster and better targeted if the multiple interfaces between science and non-scientific influences are recognized and dealt with by the individual person carrying responsibility in the energy science challenge. May this book help to cerate awareness for the interdisciplinary needed to create new and sustainable energy systems.

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