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Introduction

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1.1 A Few Words at the Beginning

Catalysis is at the very basis of life. The fact that this sentence could be read is due to the catalytic processes proceeding in our body, in this case biocatalytic processes. At the same time a heterogeneous catalytic process, the Haber–Bosch synthesis of ammonia, made it possible that the world has its current size of population. Without it insufficient fertilizer would exist and only half as many humans could live and they would have significantly less meat to eat. Catalysis is thus an essential science that finds its way into every aspect of our lives. It is commonly divided into three different disciplines, namely, homogeneous catalysis, heterogeneous catalysis, and biocatalysis. All these disciplines work according to the same underlying principles. This book therefore aims at explaining these principles while at the same time teaching each of the three disciplines as well as the engineering that is necessary to bring catalysis into industrial action.

1.2 Catalysis in a Nutshell

Catalysis is purely a kinetic and not a thermodynamic phenomenon. It is about speeding up reactions and lowering activation barriers, not about changing equilibria. Catalysis is a cycle in which reacting molecules bind to the catalyst, where they react to a product that subsequently desorbs and leaves the catalyst available for the next reaction sequence. Catalysis is thus a cycle of stoichiometric elementary reactions. Neither of these steps can be called catalytic in itself. It is the cyclic combination of events from which the catalyst emerges unchanged that makes the sequence catalytic. When different types of catalysts are used, these steps can be very different even when the starting material and the product are the same. Indeed, some processes have been industrialized with heterogeneous catalysis and then switched to biocatalysis or homogeneous catalysis and vice versa.
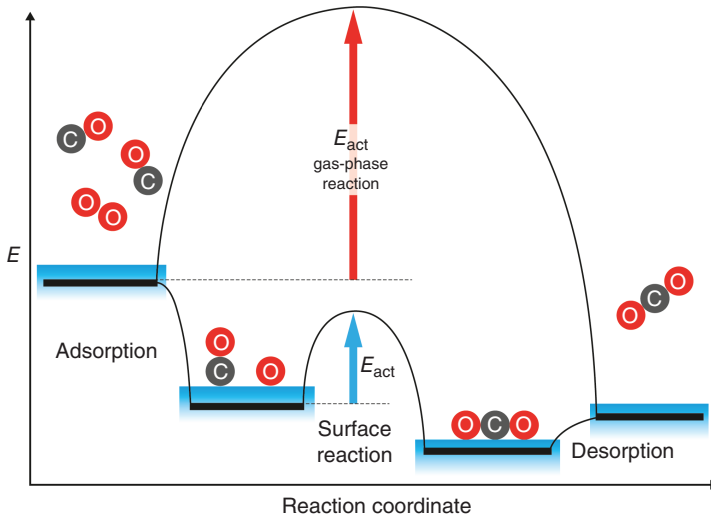
Figure 1.1 Potential energy scheme of a heterogeneously catalyzed reaction: the CO oxidation.

A reaction in heterogeneous catalysis starts with the adsorption of the reactants onto the surface. For example, let us consider the catalytic oxidation of CO on a noble metal such as platinum (Pt) (Figure 1.1). Homogeneous catalysis as well as biocatalysis operates in the same manner; however, nomenclature can be rather different as will be discussed in Section 1.4. Carbon monoxide adsorbs molecularly, while O_2 dissociates. Adsorption is an exothermic process that decreases the potential energy. Next, the adsorbed CO and O react on the surface to produce CO_2, which is weakly bound and desorbs into the gas phase, leaving the surface free for the next reaction event.

Figure 1.1 shows how the catalyst offers an alternative pathway for the reaction, with a mechanism that is more complex than the direct gas-phase reaction, but which leads to a lower overall activation energy for the reaction. Generally according to the Arrhenius Law, the rate constant, *k,* of an elementary reaction depends exponentially on the activation energy

$$k = v\,e^{-E_{act}/RT} \tag{1.1}$$

where v is the pre-exponential factor, R is the gas constant, and T is the temperature. Hence, from Figure 1.1, one realizes immediately that a decreased activation energy accelerates the reaction tremendously.

Note that the overall change in free energy is determined by the reactants and products and in no way by the catalyst. Hence, if the conversion of a gas-phase reaction under certain conditions of temperature and pressure is limited to the equilibrium concentrations of products and reactants, then a catalyst cannot alter this. A catalyst affects the kinetics of a reaction, but NOT the thermodynamics.

Another important point to note is that the catalyst offers an energetically favorable pathway not only for the forward reaction but also for the reverse one. Hence an effective catalyst used for the formation of CO_2 from CO and O_2

would also be a good choice for the reverse reaction. For example,

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (1.2)$$

The forward reaction is known as the steam reforming of methane to produce synthesis gas ($CO + H_2$), which is an endothermic reaction carried out with nickel catalysts at high temperature. The reverse reaction is the (exothermic) methanation reaction that is applied to purify H_2 from traces of CO or even to produce substitute natural gas from coal or biomass. This reaction also utilizes nickel catalysts but at temperatures much lower than the steam reforming.

Expertise in catalysis is extremely important in the chemical industry for two main reasons. By definition, catalysts enable reactions to proceed faster so that smaller reactors as well as milder conditions, that is, temperatures and pressures, can be employed. Thus, costs to achieve the chemical conversion can be reduced. However, even more important is the fact that catalysts allow enhancement of the desired conversion, without increasing the rate of formation of undesired products. In other words, selectivity of the conversion can be improved. Therefore, more useful product can be produced per amount of feedstock, limiting the production of waste as well as the need to separate targeted products from waste produced by unselective reactions. The result is that costs can be reduced, in terms of both investment and operating costs.

1.3 History of Catalysis

Without catalysis, there would be no life. All organisms in nature, including ourselves, exist by the grace of enzymes, biocatalysts, steering the chemical processes in the organisms that allow them to act at all, including self-repair and reproduction. Obviously, mankind using catalysis to make a product is much more recent than the origin of life. Still it is a long time ago and occurred without any notion of the concept of catalysis. Enzymes in yeast have been used for 8000 years or so to convert sugars, producing products such as wine, beer, and bread.

Catalysis, more specifically biocatalysis, thus has allowed us to form societies and live as civilization. Once humans started to live closely together in large groups, safe supply of water and food and the storage thereof became very important. Usage of yeast to produce alcoholic beverages and at the same time suppressing all other pathogenic microorganisms ensured relatively safe drinking supplies. Equally, bread made with yeast allowed the production of storable produce. *Lactobacillus* and similar organisms that outgrow pathogens while creating acidic media and thus suppressing all other microorganisms were and are another common application of catalysis. Yoghurt, cheese, and countless other dairy products to preserve milk and sauerkraut, salami, and many other forms of food rely on this type of catalytic formation of lactic acid. Meat was made tender by wrapping it into papaya leaves, in this case proteases from the leaves digested the meat a little making it more suitable for human consumption. All of these were performed without any knowledge of the term and the meaning of catalysis.

The concept of catalysis started to develop in the nineteenth century [1]. It was observed that ethanol could either be decomposed to acetaldehyde with a

pungent smell or to ethylene, depending on which solid was added. We now know that metals catalyze dehydrogenation, whereas oxides with acid functionality induce dehydration. A first human-designed application, again without knowing the concept at that time, was actually a *sensor* that is able to detect explosive gases. In 1817 Davy, assisted by a young Michael Faraday, discovered that a heated Pt wire would detect H_2, CO, and CH_4 in air as oxidation of these gases would produce so much heat that the wire would light up. This provided a way to detect these gases in coal mines before they would increase to levels within the explosion limits. Based on this the Miner's lamp was developed, an important safety device in coal mines at that stage. It was JJ Berzelius in 1835 who for the first time suggested a definition for the underlying mechanism and proposed the term catalysis, inspired by the Greek word for "loosen." It was proposed that the catalyst was able to induce decomposition of bodies like the components in mine gas. The concept was not essentially different from the concept of dissociative adsorption in surfaces as we know it now.

1.3.1 Industrial Catalysis

Despite the lack of understanding, the first industrial application, albeit on a very small scale as compared to today's standards, was developed in the early nineteenth century. In 1831, the production of sulfuric acid was patented, in which oxidation of SO_2 to SO_3 using finely divided Pt was a slow critical step. Much later, Pt was replaced by the much cheaper vanadium. In 1838, it was discovered that ammonia could be oxidized over Pt to produce nitric acid, which is essentially the foundation of the current process for production of nitric acid via ammonia oxidation over Pt–Rh gauzes. At that time, natural nitrate in the form of Chile saltpeter was much cheaper.

By the turn of the nineteenth century those natural nitrate resources soon ran out and N-containing salts were in high demand as fertilizers. A lack of N would have caused a major famine. Several eminent scientists have addressed this problem in the early twentieth century and Os and U were found to be active but insufficiently available. The founding father of the industrial production of NH_3 was Fritz Haber (University of Karlsruhe) and he collaborated with Baden Aniline and Soda Factory (BASF) where Mittasch led a crash program to find a cheaper catalytic material for ammonia production. They found that Fe_3O_4 from a specific mine in Sweden was very active. Impurities in that specific ore (like Na and K) were found to be responsible for this advantageous effect. Finally, Bosch was able to build an industrial process based on these findings, mastering the high pressure that is required on a large scale. The first plant was started in 1910 in Oppau, near Ludwigshafen. The process is described in somewhat more detail in Section 2.1.2.2. These developments around ammonia and nitrate chemistry were not only essential for increasing the capacity of agriculture in order to feed mankind, but also for the production of explosives, for example, in the First World War. Today more than 85% of all ammonia produced via the Haber–Bosch process is utilized to produce fertilizers.

Political and military issues have been influencing the development of specific catalytic processes over the time. Catalytic cracking (see Section 2.1.2.) of the

heavy fraction of mineral oil was developed to industrial scale in the United States in order to make available sufficient kerosene for the US Air Force in WW II. On the other side, Nazi Germany had no access to oil and produced liquid fuels from synthesis gas via coal gasification. The Fischer–Tropsch process was developed for that reason and more details can be found in Section 2.1.2.1. Later in 1970s and 1980s, South Africa developed this technology further due to the lack of access to mineral oil, which was caused by an international embargo because of their Apartheid politics. In recent times, very large investments have been made at remote oil fields, in order to convert associated stranded gas to liquid fuels, for example, in the Middle East. In China, Fischer–Tropsch technology is used in combination for syngas production via coal gasification.

The ever-increasing capacity of fuel production also induced the increasing availability of cheap feedstocks for chemicals such as ethylene, propylene, and aromatics (Benzene, Toluene, Xylene, or short BTX). Based on these platform molecules, numerous catalytic processes were developed to produce polyethylene, polypropylene, polystyrene, polyamides, and polyesters. As costs of chemicals are structurally higher than that of fuels, the added value of chemical products, or precursor of those like naphtha, is essential for the overall profitability of a refinery. Processes are therefore highly integrated and interdependent.

1.3.2 Environmental Catalysis

Environmental catalysis became important in 1970s and 1980s, with increasing concern about the environment in leading industrial countries at that time. The result was the development of new and improved processes to remove S and N from fuels (hydrodesulfurization, HDS and hydrodenitrogenation, HDN); as discussed in Chapter 2. In addition, catalytic technology was employed to clean exhaust gases of both large-scale installations like power stations (selective catalytic reduction (SCR) and DeNOx), industrial boilers, and incinerators and small-scale mobile sources like combustion engines in cars and heavy-duty trucks (three-way catalyst). More information can be found in Chapter 2. Today, these technologies are being implemented in the vast-growing metropolitan areas, facing enormous challenges to ensure air quality, in countries with rapidly growing economies such as Asia and South America.

1.4 Integration Homo–Hetero-Biocatalysis

In the early days of catalysis, Ostwald included as catalytic phenomena [2] the following:

- release of super-saturation,
- catalysis in homogeneous mixtures,
- catalysis in heterogeneous systems, and
- enzyme action

Except for supersaturation, this is exactly the scope of this book. Remarkably, the three subareas, that is, homogeneous, heterogeneous, and biocatalysis, have

been developed along different lines in the last century. Biocatalysis has been dominated by biology and biochemistry, whereas heterogeneous catalysis was inspired strongly by solid state and surface chemistry in combination with engineering and practical application. Homogeneous catalysis was developed much more along the lines of (metal-) organic chemistry. As a result of this, the subfields became detached to an important extent thereby even leading to differences in vocabulary and technical terms, see Table 1.1. We should never though forget that the underlying principles are the same and luckily the scientific community in the Netherlands decided in 1999 to invest in reconstructing the interaction among our subdisciplines. The Netherlands' Catalysis and Chemistry Conference and the Catalysis: An Integrated Approach (CAIA) course are important instruments to strengthen the understanding and cooperation between these subdisciplines. The terms used in Table 1.1 will be extensively described in the following chapters of this book and the reader is referred to this table for understanding the terminology. To point out just a few examples:

- A substrate in homogeneous catalysis and biocatalysis is identical to a reactant in heterogeneous catalysis; in the surface science subdiscipline, the word substrate is sometime used with a completely different meaning, that is, the supporting material for a model catalyst.
- With the term metal in homogeneous catalysis, normally a single metal ion is addressed, which is a typical active site in a homogeneous catalyst. A metal nanoparticle would be termed metal-black in homogeneous catalysis. In heterogeneous catalysis, the term metal is normally used to describe a metallic active phase, which could be, for example, metal nanoparticles on a support material or even bulk metals such as Pt–Rh gauzes. In biocatalysis the metal is the metal in the active site of the enzyme, catalyzing the reaction, very similar to homogeneous catalysis.

Table 1.1 Technical terms in different fields occasionally differ although they describe the same thing.

Homogeneous catalysis	Biocatalysis	Heterogeneous catalysis
Substrate	Substrate	Reactant
Decomposition	Leaves the active site	Desorption
Hougen–Watson	Michaelis–Menten	Langmuir–Hinshelwood
Metal black	–	Metal
Metal	Metal	Metal$\cdots$ion, oxide, compound
Oxidative addition	Oxidative addition	Dissociative adsorption
Association	Docking	Adsorption
TON	TTN	TON
TOF	TON	TOF

TON: turnover number; TTN: total turnover number; TOF: turnover frequency.

- Remarkably, the first interaction of a catalyst with a reactant is called adsorption in heterogeneous catalysis: this is termed from the perspective of the reactant (or substrate). In contrast, in homogeneous catalysis, the complex catalyst is chosen as perspective and the substrate (reactant) therefore associates with the catalyst. In biocatalysis, the substrate docks into the active site.

Catalytic processes based on each of the three subdisciplines have strengths and weaknesses (see Table 1.2). Heterogeneous catalysis involves relatively robust materials that can be handled easily, can be easily separated from products, and can withstand high temperatures so that the reaction rates can be very high by operating at high temperature. However, the control on the active site is normally not very good because the structure of sites at the surface is hard to control; as a result, activity (at mild conditions) and selectivity are generally inferior when compared to homogeneous catalysis and even more when compared to

Table 1.2 General strengths and weaknesses of the different types of catalysts.

Property	Homogeneous catalysis	Biocatalysis	Heterogeneous catalysis
Catalyst	Molecule, complex	Enzyme, molecule	Solid
Medium	Generally liquid	Generally liquid	Gas or liquid
Activity	High	Very high	Variable
Selectivity	High	Very high	Variable
Reaction conditions	Mild	Mild	Harsh
Service life of catalyst	Variable	Variable	Long (most cases)
Diffusion problems	None	None	High
Product separation	May be problematic	May be problematic	Easy
Catalyst recovery	Expensive	Variable	Not necessary
Tunability	High (via ligands)	High (via genetics)	Low (via promotors)
Mechanistic understanding	High	High	Less
Scale of application	Many small processes	Small and medium scale	Large processes
Application	Fine chemicals, specialties	Fine chemicals, food	Bulk chemicals, fuels, environmental clean up
Type of process	Batch	Batch	Continuous
Scientific discipline	Chemistry	(Bio)chemistry	Mainly physical chemistry and chemical engineering

biocatalysis. Table 1.2 provides a very generalized description. The actual choice for a process using a specific catalyst is made in practice based on all factors influencing the costs, including both investments and operation cost. It is clear that such an evaluation is very specific for each process, but in general will be influenced by the following:

- the size of reactors, heat exchangers, and separation units,
- costs of construction material in view of corrosion, temperature, and pressure,
- complexity of any separation required,
- cost of the catalyst itself,
- integration with facilities onsite,

and many, many more.

Table 1.2 shows that all types of catalysis have advantages and disadvantages. Which catalyst is applied is often dependent on the current level of knowledge. Historically acetic acid (vinegar) was always produced via fermentation and biocatalysis. With an increase of demand approaches via ethylene with heterogeneous catalysis were investigated but did not reach the market. Instead, carbonylation of methanol via homogeneous catalysis turned out to be the best current approach. Three different metals are commonly used, Co in the BASF process, Rh in the Monsanto process (Figure 1.2), and Ir in the Cativa process. With a change in feedstocks that takes place with biomass as starting material these processes might, however, again be replaced [3].

Ethanol is also historically a product of fermentation and still is. However, ethanol and other small alcohols are today produced via heterogeneous catalysis, typically with heterogeneous acids. Indeed, the hydration of isopropene via heterogeneous catalysis is one of the oldest bulk petrochemical processes that had already started in 1920s. Ethanol was also produced like this since the
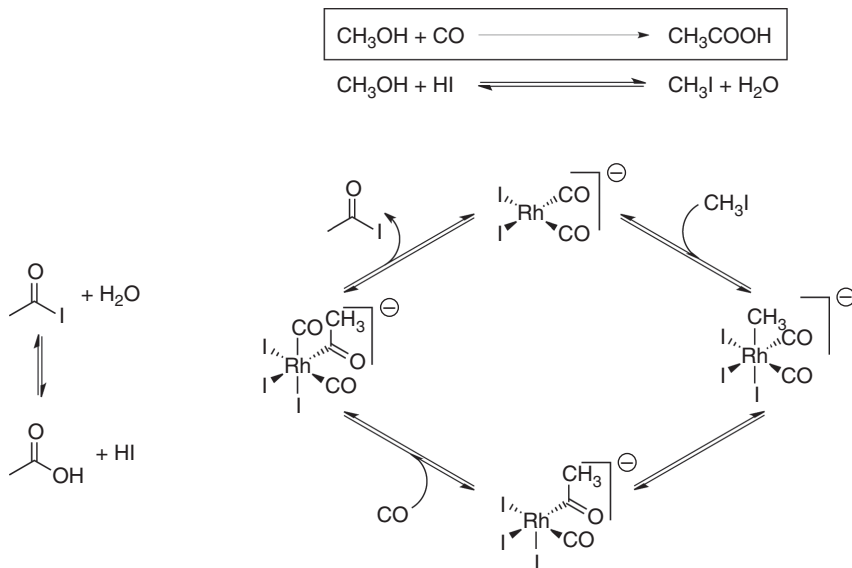

Figure 1.2 The Monsanto acetic acid process.

1950s, in addition to the classical fermentation for consumption. More recently with the advent of biomass as a feedstock, a movement back to fermentation is taking place.

Acrylamide, the monomer of polyacrylamide, is another molecule that demonstrates that the choice of catalysts is not always obvious. Initially, the hydrolysis of acrylonitrile to acrylamide was done with a homogeneous catalyst (sulfuric acid). This was then substituted with a heterogeneous catalyst, since this allowed continuous processes and catalyst recycling. However, a selectivity issue remained, as acrylic acid was also produced next to acrylamide leading to a difficult product separation. Today, this process is catalyzed by an enzyme. The enzyme nitrile hydratase catalyzes only the acrylamide formation but not the next step to acrylic acid. With a selectivity >99.99%, conversions >99% are obtained. Since the catalyst is immobilized the separation and reuse is straightforward [3].

A good knowledge of all the types of catalysis is thus essential to make the right choice and to find the catalyst that is optimal for the process under investigation. All the types of catalysis are used industrially and all have its own distinct advantages. A beautiful example where all the types of catalysis were used to their full strength is the synthesis of the antiflu drug Tamiflu (developed by researchers at F. Hoffmann–La Roche, Figure 1.3). Starting from a very cheap
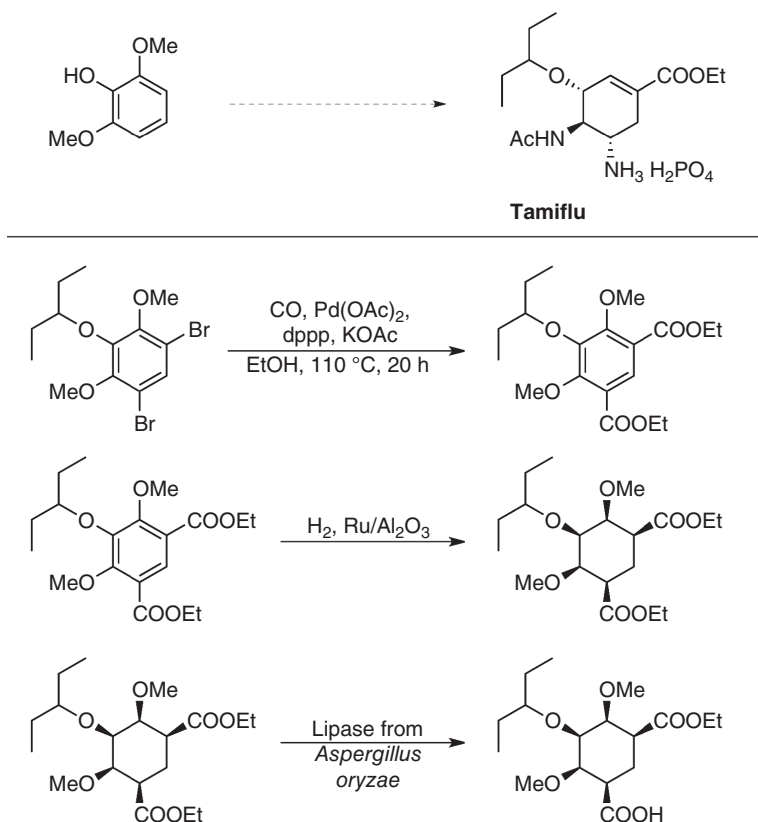

Figure 1.3 Hoffmann–La Roche approach for the synthesis of Tamiflu.

achiral aromatic compound, homogeneous catalysis was utilized to introduce two carbonyl groups and provide the essential ester group of Tamiflu. Then a very clean catalytic hydrogenation with a heterogeneous catalyst led to a prochiral molecule, abolishing aromaticity on the way. Chirality was then introduced with a highly selective enzyme, generating five stereocenters in one single step. All these were only possible by applying each type of catalyst for its particular strengths [4].

1.5 Research in Catalysis

1.5.1 S-Curve, Old Processes Improvement Is Knowledge Intensive

Since catalysis started to develop in the nineteenth century (Section 1.3), it developed in different directions and with different time frames. First mainly (though not exclusively) focusing on fossil resources followed by environmental catalysis and more recently on the use of renewable resources and CO_2 as feedstock. As a result, the development of catalysts and catalytic processes is in different phases. These phases are often described by an S-curve (Figure 1.4).

For new processes and catalysts, initially a significant research effort is needed to explore and understand the new field. When successful, the research makes a leap and improvements are achieved at a higher rate. In the consecutive step, the field reaches maturity and significant efforts are again needed to make small improvements. The profitability of a process follows more or less an inverse trend. In the beginning large investments in research are needed to advance a field, when more maturity is reached the process becomes more economically viable and therefore profit is made. In the middle stage, however, there is a period that is also called "the valley of death." In the initial stage, at the beginning of the S-curve, large research efforts are needed; however, the need for investment is relatively moderate. At the end of the S-curve, the process is proven to be profitable and therefore return on investment (ROI) can be well calculated. In the middle stage,
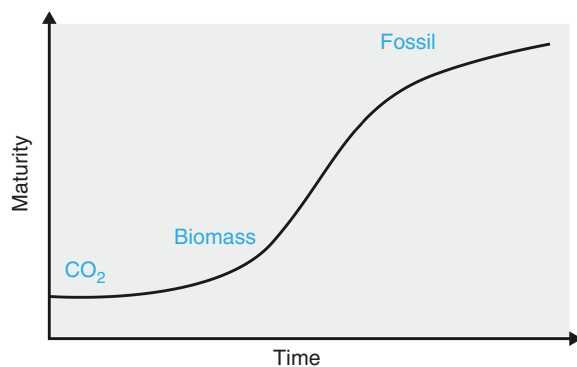

Figure 1.4 S-curve for research in catalysis.

large investments are needed in pilot and demo plants, yet the process is not mature enough to secure the ROI. This is the phase that is difficult to overcome.

Reasoning from a feedstock point of view, that is, fossil, biomass, and CO_2, it is reasonable to state that they are in different phases on the S-curve, the conversions of fossil sources are in general mature and at the end of the curve. Kindly note that large research efforts are still ongoing in that field, but improvements are small though economically very relevant. The use of biomass is at the bottom of the S-curve. New insights have emerged in recent years though the major breakthrough has not yet been made. The use of CO_2 is at the moment at its dawn. It is regarded as a potential source for carbon in fuel and chemicals in the future, but its potential is not fully clear yet.

1.5.2 Interdependence with Other Fields

To go all the way from feedstock to products a number of steps are needed of which the catalytic conversion step is a crucial one, though it is not the only one. The feedstock has to be collected, transported to the conversion plant (by pipeline, boat, truck, etc.), converted to the desired products, and finally the product has to be delivered to the customer/consumer. The logistic part of the production falls outside the scope of this book, though it shows that catalysis blossoms when interacting with other fields. Here, we will focus on the conversion part, that is, convert the feedstock to the desired product. In addition that is not a single, isolated, field. To be able to convert the feedstock it has to be loaded into a reactor, the feedstock, optionally after cleaning, has to be converted, and the product has to be separated from byproducts or unconverted feedstock. Therefore, reactor technology, catalysis, and separation are the fields that need to collaborate closely in order to find the most efficient way to the desired product. A good process design is crucial in that respect.

Conversely, a process design can also identify the bottlenecks for the other fields of science to solve. For example, as discussed above, HDN and HDS are important catalytic processes to clean a feedstock before it can be converted in a catalytic process. The HDN and HDS processes are needed to protect the catalyst from poisoning. Thus, when new N and S tolerant catalysts can be developed one has to rethink the whole process to make it more efficient.

The issue of effective process design is even more relevant for biomass conversion. Since biomass conversion is still at the bottom of the S-curve, it is still a question as in which technology is most efficient. For example, when working with aqueous solutions, not uncommon in biomass conversion, it is beneficial to make a product that is apolar and separates out easily from the reaction mixture to lower separation costs. In addition, when looking at the molecular structure of biomass (cellulose, lignin, etc.), which is highly functionalized, the conversion to functionalized products should be possible with only limited energy input. This would then allow conversions in small-scale plants, which need rethinking of the whole processing chain, as now we are using large-scale plants. The latter is due to the fact that often economy of scale applies due to the need of heat exchangers that are more effective on larger scales.

1.5.3 Recent and Future Issues

Different scenarios on the development of the human population exist (Figure 1.5). It is realistic to expect that about 10 billion people will live on the earth at the end of the twenty-first century with ever-increasing wealth. To keep our planet inhabitable, it is therefore crucial that we use renewable resources in a sustainable manner. Catalysis is one of the key elements to achieve this.

Currently, our infrastructure and needs are aligned with the use of fossil resources. Oil refineries are energy efficient and dedicated to make the fuels and chemicals we currently need. However, the feedstock is not sustainable; thus on the long term, the desirability of the use of fossil resources is questionable.

1.5.3.1 Biomass

Currently, the biobased economy is often discussed as a driver of research. When switching from fossil resources to biobased renewable resources (in a proper way), less amount of CO_2 is emitted to the atmosphere thus reducing global warming. Moreover, as the resources of choice in that case are renewable we do not deplete the scarce resources of our planet. Wubbo Ockels (the first Dutch astronaut) stated in one of his last letters "The problem is that Humanity needs to find a sustainable balance with its environment, with our home the planet Earth and its Nature."

Biomass on the other hand is renewable but has a completely different chemical composition and structure when compared to the fossil resources. Fossil resources mainly consist of C and H, while biomass also contains significant amounts of O (Table 1.3). The latter is a challenge when trying to make the molecules present in the biomass compatible with the current infrastructure and need for fuels. In that case, the biomass needs to be defunctionalized, that is, the oxygen which increases the energy content of the remaining molecules
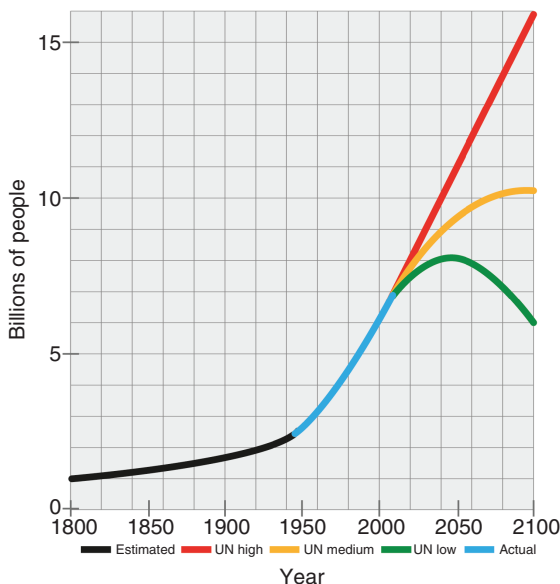

Figure 1.5 Potential developments of number of inhabitants on the earth. Adapted from http://upload .wikimedia.org/wikipedia/ commons/thumb/7/77/World-Population-1800-2100.png/ 587px-World-Population-1800-2100.png.

Table 1.3 Comparison of oil and biomass composition.

Oil		Biomass	
Element	Percentage (%wt)	Element	Percentage (%wt)
C	83–87	C	50
H	10–14	H	11
N	0.1–2	N	0.5
O	0.1–1.5	O	35
S	0.5–0.6	S	0.1
Metals	<0.1	Ash	2
		Dry biomass 50% moisture	
		(http://www.treepower.org)	

needs to be removed. However, energy has to be invested to remove the oxygen. When that energy originates from renewable resources (wind or solar) this can be viable from a renewable point of view. Conversely, one can ask the question why do we not use the renewable resources directly?

On the other hand, when talking about chemicals often functionality is desired in the feedstock molecules. For example, carboxylic acid functionality and amino groups are needed to make nylon from adipic acid and hexanediamine. From that point of view, biomass is a more viable resource as it already contains functionalities. One should also ask the question whether the currently utilized molecules are the most desired ones or whether new molecules should be made from biomass. This, however, needs a change of mindset about which molecules we need and which process we need to make them. This might conflict with the currently existing infrastructure, which were installed with high investment cost, thus changes to biobased feedstocks/products might be slow for financial reasons. When installing new capacity, however, we should think about the most effective way from a renewable and financial point of view.

1.5.3.2 CO_2 as a Feedstock

Using CO_2 as a feedstock is an interesting approach to address the major environmental issues that we have today while producing chemicals. When CO_2 is converted to fuels and chemicals, the increase in CO_2 levels in the atmosphere is slowed down or the levels can even be decreased. To make that possible, challenging hurdles have to be overcome. For example, when we want to decrease the CO_2 levels in the atmosphere effective capture methods are needed. In addition, a grand challenge is how to effectively convert CO_2 to other products. Carbon-dioxide is thermodynamically a very stable molecule, thus energy is needed to valorize it. In fact, C–O bonds have to be converted to C–H bonds and C–C bonds, that is, reductions are needed.

For these reason, electrochemistry and photochemistry are revived again. Recent developments in the fields of solar energy (photovoltaic) and wind energy may indicate future availability of cheap electrical power, in contrast to the

normal perception that electrical power is relatively expensive. The consequence would be that conversion of electrical power to fuels and chemicals might see an important revival, for example, via electrochemistry. In photochemistry, light is used to generate electrons that can be used to reduce CO_2. Thus, photocatalysis is again, certainly at academic level, becoming an important issue. The energy needed for these processes needs to come from renewable resources such as to make the processes sustainable.

Another option to use CO_2 as feedstock is to use it as building block in chemical synthesis. Examples are the reactions of CO_2 with alcohols and polyols, amines, olefins, dienes, and alkynes, to form carboxylates, carbonates, and carbamates. However, also in that case energy is needed to convert the CO_2, maybe not directly to drive the specific reaction but the energy is then already introduced in the reactant by the introduction of reactive bonds.

The challenges we have sketched here are in no way complete, and the future may take humanity in yet another direction. One thing, however, is obvious: Catalysis will help us to face those challenges.

1.6 Catalysis and Integrated Approach or How to Use this Book

This book evolved out of the annual course *Catalysis: an Integrated Approach* (CAIA). The chapters are written by the teachers of the course, and each chapter can be read on its own to get up to speed on its topic. This is also the common way of presenting catalysis, separated and not integrated. The real value of this book is that, as we hope, all the chapters also show the link to the other fields of catalysis and that all topics are presented side by side. This eases cross reading. The aim is that all the chapters can be read also by non-experts in the field allowing to quickly gain insight into the opportunities of each type of catalysis as to allow for the choice of the best catalyst and the matching reactor.

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