1
Catalysis in Perspective: Historic Review

Rutger van Santen

1.1
History of Catalysis Science

1.1.1
General Introduction

Catalysis as a scientific discipline originated in the early part of the last century. Earlier, the unique feature of a catalytic substance, namely that when added in small quantities to a reaction it affects its rate and selectivity but is not consumed, had become widely recognized, and many applications had been developed. Only after chemical thermodynamics had been defined did a rational approach to discover new catalytic processes become possible. Thermodynamics would define the proper conditions at which a material should be tested as a catalyst and catalytic turnover would be expected. Ostwald, one of the founding fathers of chemical thermodynamics, introduced thermodynamics into the physical chemical definition of a catalyst, specifying that it is a material that will leave the equilibrium of a reaction unchanged.

The past century can be viewed as the age of the molecularization of the sciences. It took nearly a century before the molecular basis of catalytic processes, now widely applied at very large scale, became understood. The Haber–Bosch process of ammonia synthesis was discovered early in the twentieth century once the thermodynamics of this process had become properly understood. The Nobel Prize to Ertl in 2007 recognized his discovery of the molecular principles of this reaction.

The three scientific disciplines that are essential to catalysis: chemical engineering, inorganic chemistry, and organic chemistry, which developed in the past fairly independently, now have a common basis (see Figure 1.1).

The chemical tradition of the nineteenth century had culminated 100 years earlier in the Nobel Prize for Sabatier for catalytic hydrogenation, useful because coal had made the production of hydrogen cheap. Sabatier formulated the principle that the reaction intermediates formed at the surface of a catalytic material should have an intermediate stability. When too stable they would not decompose, when too unstable they would not be formed. This molecular view of the catalytic

Catalysis: From Principles to Applications, First Edition. Edited by Matthias Beller, Albert Renken,
and Rutger van Santen.

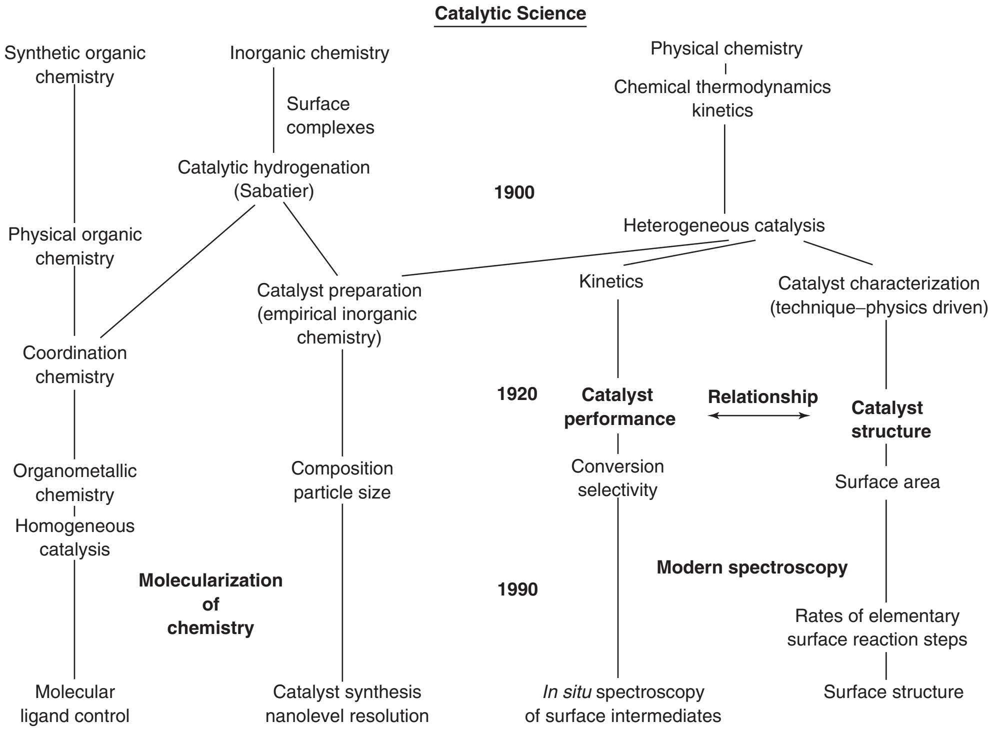

Figure 1.1 The three branches of catalysis history.

reaction, not as a single reaction but as a cycle of reaction steps, in which intermediate complexes between a catalyst and a reagent are formed and then decay, was particularly modern. Sabatier's principle is the formulation of the molecular basis of catalytic action and complements Ostwald's physical chemical view.

Current state-of-the-art physical chemical instrumentation and computational and molecular chemistry provide a basis for the formulation of a molecular theory of catalysis. This basis will be presented in the first three chapters.

1.1.2

Heterogeneous Catalysis: the Relationship between a Catalyst's Performance and its Composition and Structure

Kinetics provides the basis to the physical chemical description of catalytic reactivity. Reaction engineering is the discipline that connects reactor performance with the chemical reactivity of the catalyst. The level of accuracy to be obtained is highly dependent on the accuracy, sensitivity, and compatibility of measuring technique with catalytic reactor operation. It is essential to understand the difference between performance parameters, which are caused by such phenomena as heat and mass transfer, and features of the catalytic reaction, which in turn are due to the chemical reactivity of the catalytic material. This is the difference between extrinsic and intrinsic kinetics, to be discussed in Part I.

The link between chemical kinetics and molecular activation at the catalyst surface is through the mechanism of the catalytic reaction. This implies a physical organic chemistry type of understanding of the reaction paths of molecular transformations that happen when the reaction proceeds in its catalytic cycle. Transient and isotope-labeled kinetic studies as well as *in situ* spectroscopic measurements are the experimental tools. To obtain detailed molecular information, such studies often have to limit themselves to the investigation of a single elementary step of the overall catalytic reaction. The integration of such information in order to understand the kinetics of the complete catalytic cycle usually involves the lumping together of properties of many elementary reaction events, which causes the physical chemistry of kinetics and molecular understanding to be often indirectly related. Agreement between prediction and experiment is important as a tool, but cannot be considered the ultimate proof of the validity of a proposed mechanism.

This state of affairs is dramatically improved by advances in computational modeling of catalytic chemistry, which currently enables the prediction of rate constants of elementary reaction steps and discrimination between mechanistic options of reaction routes. The mechanistic discussions in later chapters will demonstrate this.

A central theme in the science of heterogeneous catalysis has been and still is the characterization of the catalytic material at the level of detail relevant to its performance.

Similarly to the direct access to the mechanism of reactions, molecular characterization of the catalyst surface also has long been beyond direct reach of experimentalists. Due to the heterogeneous nature of a catalyst's particles this is still not always completely possible, but for model type catalysts a molecular description is becoming possible.

It is becoming evident that ultimately transformations of the catalyst structure are intimately related to the chemical transformations they induce and the influence of the reaction medium. Thus surface changes and surface chemistry are intimately coupled. Again, advanced spectroscopy in combination with computational approaches is getting to a stage where definitive study becomes possible.

Probing the molecular basis of catalysis generated the need to study model systems to validate theory and experiment at their respective time and length scales. It gave rise to the surface science approach in catalysis, with a corresponding generation of catalytic surfaces and surfaces of increasing molecular definition. This, coupled with the considerable parallel advances in coordination chemistry, metal organic chemistry, and homogeneous and molecular biocatalysis, gives rise to new generations of catalysts of increasing complexity, but also increasingly better molecular. This not only leads to catalysts of increased selectivity, stability, and energy efficiency, but also helps fundamental progress in catalysis. Definition of reactivity descriptors, which are of molecular refinement, becomes possible. The history of catalysis shows this in the progression of techniques for characterization and kinetics modeling approaches.

The first important characterization tool next to chemical composition was structural characterization. The Brunauer-Emmett-Teller (BET) and later T-plot techniques were developed to determine catalyst surface area and porosity structure. These methods were based on thermodynamics, and hence could not provide molecular information. X-ray scattering techniques were developed to characterize particle size and kind. A major advance was the use of electron microscopy. The ongoing development of spectroscopic techniques, such as photo-emission and synchrotron-based methods, has only recently made it possible to analyze complex working catalysts at a nanometer scale.

Truly molecular information needs access to model systems and model conditions in order to apply spectroscopic techniques with atomic resolution. This very important branch of catalysis found its early start in Langmuir's surface science studies in a vacuum. Later this was brought to high levels of sophistication especially by the schools of Somorjai and Ertl. It is the data from such studies that provide validation of the now also well-established discipline of computational catalysis. In the next chapters the fundamental insights on catalyst reactivity provided by these approaches will be given.

The formulation of kinetics underwent similar changes. A proper description of the kinetics of a catalytic system is crucial to the design of catalytic reactor systems. An understanding of the relationship between the volume of a catalyst and its performance is fundamental. Knowledge of porosity and surface area is of direct engineering relevance. Whereas the equations can be mathematically complex, the basis of kinetics up to the present is empirical. Over the past century kinetic models, useful for engineering purposes, were designed by fitting parameters to experimental measurements. To improve such models, mechanistic assumptions about the reaction network had to be made. These became more and more refined with the increasing understanding of the physical chemistry of catalytic reactivity.

The simplest kinetic equation is the power law rate expression that relates the rate of the reaction with the concentration of reactants and products. As we will see in the next chapter the parameters of such power law expressions depend in principle also on the concentration of reacting molecules and can be expected to be only valid over a limited concentration, pressure, and temperature regime.

The Langmuir–Hinshelwood–Watson–Hougson (LHWH) expressions, which do not use the assumption of the power law concentration dependence, can be used to derive the simpler and more easy-to-use kinetic expressions. The LHWH expressions need the explicit assumption of a reaction mechanistic network. They also involve the assumption that most reaction steps are equilibrated and only one reaction is not equilibrated (often called the *rate-limiting step*). In addition, the surfaces are usually assumed to be uniform, and, most importantly, in the models the total number of reaction sites is maintained constant. For this reason the LHWH expressions are the equivalent of the Michaelis–Menten expression used in enzyme and homogeneous catalysis. The parameters in the LHWH expressions that are fitted to experiment are to be considered lumped parameters, since many details of the elementary surface reactions are ignored.

Microkinetics is the kinetics approach that takes full account of the elementary reaction rate expressions deduced from catalysis studies at the molecular level. Eyring's transition state expressions are used. No assumption is made about equilibrated and non-equilibrated reaction steps.

Ultimately, Dynamic Monte Carlo methods have been developed that can include non-uniformity of surfaces, overlayer phase formation, and even surface reconstruction effects. No mean field approximation of uniform surface concentrations, as made in the other methods, is necessary in this case. Such methods are useful to deduce kinetic parameters valid in particular concentration regimes to be used in other simpler-to-handle approaches.

The ongoing molecular understanding of the chemistry and characterization is also impacting the molecular level design of heterogeneous catalytic systems. Most important was the insight, which gained general support, that the reactivity of a surface and that of related molecular complexes can be quite similar. This brought heterogeneous catalysis into the heart of molecular catalysis. Here we now see an important cross-fertilization of the intrinsically molecular approach of coordination complex chemistry and the increasing importance and refinement of homogeneous catalysis in the second half of the last century.

Whereas the early heterogeneous catalysts were simply metal powders, not much later they became materials with highly dispersed catalytically active components on high-surface supports. Control of composition, size, and shape of catalytically active particles and of catalyst support morphology gave rise to important improvements in the catalytic performance. This can be viewed as one of the main benefits of continued research aimed at understanding the relationship between catalyst performance and its structure.

There are many examples of the sustained gradual improvement in catalyst performance that occurred over many years. The introduction of microporous solid acidic zeolites instead of non-structured clays as catalysts for catalytic cracking of oil saved society a significant fraction of crude oil, that otherwise would have been converted into residual coke. In chemicals production a familiar example is the production of ethylene epoxide by a silver-based catalyst. In the course of 50 years the selectivity improved from initially 40% to the current 90% with large savings in ethylene that otherwise would have been combusted.

Catalyst preparation methods were based on increasing understanding of the chemistry of the often complex reaction mixtures and of the inorganic chemistry of their reaction with catalyst supports. Molecular catalysis gave rise to molecularly defined immobilized systems and the use of well-defined clusters or complexes in catalyst preparation. Zeolites, with their microscopic channel structure that is atomistically defined, can be considered to be an example of the ultimate molecular heterogeneous catalyst.

1.1.3
Homogeneous and Enzyme Catalysis

The first molecularly defined catalyst was the Co carbonyl hydroformylation catalyst discovered by Roelen in 1938. Its mechanism, defined in physical organic terms, was unraveled in the 1960s by Heck and Breslow, and it was later developed commercially by Shell.

Earlier, mercury sulfate had been industrially applied for the conversion of acetylene to acetaldehyde. Later, in the 1950s, the Wacker process of selective oxidation of ethylene catalyzed by the Pd/Cu system was introduced.

The Ziegler–Natta invention of an ethylene and propylene polymerization catalyst in the 1950s, based on $TiCl_3$, signaled the beginning of well-defined (immobilized) coordination complexes serving as catalytically active species, in parallel with the development of metal–organic chemistry.

This development was crowned by Wilkinson's discovery of homogeneous hydrogenation in 1965. The catalyst, $RhCl(PPh_3)_3$, consists of a single metallic center stabilized by triarylphosphines. The unique feature of such organometallic complexes is that they can be manipulated molecularly by variation of the ligands. With their invention the field of molecular catalysis has been expanded from the organic chemist's realm into metal-based catalysis. Catalyst design through development of physical chemical approaches, ligand synthesis, and computational modeling techniques has become one of the outstanding features of this branch of catalysis.

These developments have provided the basis of several large-scale homogeneous bulk industrial processes. Examples are the Rh-based carbonylation of methanol and hydroformylation processes. More recently we see the development of metathesis applied, for instance, in the ring-opening polymerization process of Huels, and enantiomeric catalysis due to the invention of highly enantiomeric ligand systems, as for the production L-Dopa by Monsanto.

A special issue in homogeneous catalysis is separation of catalyst from product after reaction, and for this there are unique developments and applications of biphasic systems and membrane reactors.

Whereas biocatalysis has been used widely in fermentation processes from the early beginning of mankind, the science of biocatalysis only started when Sumner and Northrop were able to crystallize an enzyme, the molecule active as a biocatalyst in the living system, and identified it as a protein. The protein acts as the complex ligand of the catalytically active center, that can be an organic acid or base, a metal, or an inorganic metallic complex. Variation of the protein composition far from the actual catalytic site can have a major effect on catalyst performance. Unique to enzyme catalysis is multipoint contact and activation of a substrate molecule when this is adsorbed into the interior of the enzyme.

Very early in the nineteenth century, Willstätter discovered catalases and peroxidases that activate hydrogen peroxide, and Summer concentrated on urease that decomposes urea.

One of the early bulk processes that employ a hydrolase enzyme is the Mitsui Toatsu process that converts acetonitrile into the corresponding amide.

Modern biomolecular chemistry has a major impact on the design and improvement of biocatalytic systems through the use of combinatorial and recombinative techniques that allow for DNA reshuffling. Such evolutionary molecular biological techniques have been developed especially for application to fine chemical synthesis. Mutations are introduced through the biochemical polymer chain reaction or other random chain reactions. This approach has led to the development of bacterial lipases with significantly enhanced enantioselectivity.

Differently from the design approaches in homo- and heterogeneous catalysis, in this approach to catalysis no mechanistic information on the catalytic reaction is used to optimize the system. The desired catalyst is found by feedback of the information obtained by screening into the selection of the bacteria possessing the desired gene sequences [1].

1.1.4
Important Scientific Discoveries

To give a historic illustration of the scientific advances that gave rise to the science of catalysis as we now know it, we have listed in this section the relevant Nobel prizes. The Nobel prizes for heterogeneous catalysis are followed by the recognition of discoveries in coordination chemistry and biochemistry.

- 1909 – W. Ostwald, for his work on catalysis, and for his investigations into the fundamental principles governing chemical equilibria and rates of reactions.
- 1912 – P. Sabatier, for his method of hydrogenating organic compounds in the presence of finely divided metals whereby the progress of organic chemistry has been greatly advanced in recent years.
- 1918 – F. Haber, for the synthesis of ammonia from its elements.
- 1931 – C. Bosch and F. Bergius, in recognition of their contributions to the invention and development of chemical high-pressure methods.
- 1932 – I. Langmuir, for his discoveries and inventions in surface chemistry.
- 1956 – C. N. Hinshelwood and N. N. Semenov, for their researches into the mechanism of chemical reactions.
- 1963 – K. Ziegler and G. Natta, for their discoveries in the field of chemistry and technology of high polymers.
- 1973 G. Wilkinson and E. O. Fischer for pioneering work on the chemistry of the organometallic so-called sandwich compounds.
- 1983 – H. Taube, for his work on electron transfer reactions, especially in metal complexes.
- 1989 – S. Altman and T. Cech, for their discovery of the catalytic properties of RNA.
- 1993 – K. B. Mullis, for his invention of the polymerase chain reaction.
- 1994 – G. A. Olah, for his contributions to carbocation chemistry.

- 2001 – W. S. Knowles, R. Noyori, and K. Barry Sharpless, for their work on chirally catalyzed hydrogenation reactions and for the work of KBS on chirally catalyzed oxidation reactions.
- 2005 – Y. Chauvin, R. H. Grubbs, and R. R. Schrock, for the development of the metathesis method in organic synthesis.
- 2007 – G. Ertl, for his studies of chemical processes on solid surfaces.
- 2010 – R. F. Heck, E. Negishi, and A. Suzuki, for palladium-catalyzed cross-couplings in organic synthesis.

The word catalysis is mentioned four times during a period of nearly 100 years – first, in the context of heterogeneous catalysis, then biocatalysis and homogeneous catalysis, and recently for application in organic synthesis. Before 1963 no research award was given for the use of coordination complexes in catalysis. In biocatalysis the first Nobel Prize was in 1946 for crystallization of an enzyme (Sumner, Northrop, and Stanley), followed by Kendrew and Perutz's (1962) Nobel Prize for crystallographic studies of hemoglobin.

It is interesting to realize that the increased understanding of the molecular mechanism in homogeneous and biocatalysis came earlier than it did in heterogeneous catalysis.

There are many factors that contribute to the recognition of a Nobel Prize award. It is interesting to ask the question whether for catalysis there are other breakthrough developments that possibly are equivalent at least in impact and originality. Below, a list of such discoveries essential to the advancement in catalysis can be found. They are important because they often are basic to the development of new industries or new catalytic processes:

- F. Fischer and H. Tropsch (1926). Oligomerization of hydrocarbons from CO – heterogeneous catalysis.
- V. Ipatieff and E. Houdry (1930). Amorphous solid acid catalysts – catalytic cracking.
- (1930) Reducible vanadium oxide catalysts for benzene oxidation, earlier discovered for SO_2 oxidation.
- T. E. Lefort (1931). Silver-catalyzed epoxidation of ethylene – a heterogeneous process.
- H. Pines (1940). Superacid catalysis (liquid phase) – alkylation.
- O. Roelen (1938) and W. Reppe (1941). Hydroformylation, carbonyl chemistry, and homogeneous catalysis.
- V. Haensel (1940). Bifunctional heterogeneous catalysts (catalytic reforming).
- J. Smidt, WACKER (1959). Homogeneous oxidation of ethylene by oxygen by Pd-Cu oxidation redox couple.
- R. K. Graselli, SOHIO (1955). Mixed oxides for selective oxidation and ammoxidation.
- R. L. Banks and G. C. Bailey (1964). Heterogeneous metathesis by supported oxide clusters.
- C. J. Plank and E. J. Rosinski, MOBIL (1968). Zeolite catalytic cracking.

- H. P. Wulff and F. Wattimena, SHELL (1969). Heterogeneous Ti-catalyzed epoxidation.
- W. Keim, SHELL (1972). Shell Higher Olefins Process.
- C. D. Chang, A. J. Silvestri, and W. H. Lang, MOBIL (1972). Methanol to gasoline, ZSM-5 zeolite catalyst.

Before 1900 we have two important inorganic chemicals produced by catalytic processes:

- Sulfuric acid by the lead chamber process (NO_x) or contact process (Pt).
- Chlorine from HCl by the Deacon process ($Cu/ZnCl_x$).

Early in the nineteenth century we have the invention of electrocatalysis, for which Faraday gave the first scientific basis:

- The invention of metal-catalyzed hydrolysis, oxygen reduction, and the fuel cell.

Also in the early part of the nineteenth century there are important inventions of applications of heterogeneous catalysis. Famous are Davy's miner's lamp (based on catalytic oxidation by Pt) and the lamp by Döbereiner (this was a Kipp's apparatus for hydrogen generation combined with a Pt catalyst for oxidation). Berzelius was inspired by acid- and base-catalyzed hydrolysis reactions.

The first half of the twentieth century is dominated by the development of heterogeneous hydrogenation processes (NH_3 and hydrocarbon-related chemistry). Hydrogen was now available from coal. High-pressure continuous processes were developed through the use of this technology. This can be considered to be the origin of reactor engineering as we now know it.

Note the early discovery of heterogeneous catalytic hydrogenation and the discovery of homogeneous catalytic hydrogenation 60 years later by Wilkinson – similarly the early discovery by Banks *et al.* of the heterogeneous catalysis of the metathesis reaction and the 30-years-later discovery of homogeneous metathesis.

1.2
The Development of Catalytic Processes: History and Future

The technological development of catalysis shows an intimate relationship between important political and societal developments and the exploitation of new catalytic technologies. The relationship between scientific discovery and its use in society is complex. Earlier we discussed highlights of catalytic advances; here we will provide a historic list of important industries based on catalysis (Table 1.1).

We have three columns. In the first column we indicate the major societal issues of that moment, for instance, the changing uses of raw materials. We recognize the transitions from coal to oil and natural gas. There also the two World Wars that had a major impact on the development of particular technologies. At the end of the last century there were oil crises and needs for environmentally friendly techniques. In the early part of this century the issues of climate change generated

Table 1.1 The history of catalytic processes.

	Catalyst	Process
1900	Noble metal	Hydrogenation
1910 World War I	Promoted iron	Nitrogen to ammonia
		Synthesis gas to methanol gasoline
1920	Sulfides	Desulfurization–denitrogenation
1930 Automobiles	Solid acids	Catalytic cracking
1940 World War II	New acid catalysis	Synthetic kerosene
	Superacids	Alkylates
	Anionic catalysis	Synthetic rubber
1950	Coordination catalysis	Polymers
1960 Petrochemical industry	Bifunctional catalysis	Hydrocracking
	Zeolites	Catalytic cracking
	Reducible oxidic systems	Selective oxidation
1970 Energy crisis	Methanol to gasoline	Novel synthetic acidic zeolites
	Synthesis gas to chemicals	Organometallic complexes
1980 Environment	Noble metal alloys	Exhaust catalysis
	Mixed oxides	Stack gas treatment
	Molecular heterogeneous catalysis	Fine chemical catalysis
	Catalytic organic chemistry	
1990 Environment	Immobilized enzymes	Enantiomeric catalysis
	Organometallic complexes in nano/mesoporous materials	
	Supported reducible oxides	NO_x, SO_2 reduction
	Zeolitic redox systems	N_2O utilization (Panov reaction)
Raw materials: natural gas and coal	Reducible mixed oxides	Selective alkane oxidation and ammoxidation
	Pt/Rh	Alkane dehydrogenation; synthesis gas
	Ga, Zn in zeolites	Alkane to olefins and aromatics
	$Si_xAl_{1-x}(PO_4)_2$ zeolitic systems	Methanol to olefins
	Co nanoparticles	Synthesis gas to hydrocarbons
2000 Climate	Electrocatalysts	Fuel cell
	Cr/molten salts	Glucose to diesel
	Early transition metals	Hydrogen storage
	Inorganic oxides	CO_2 storage and activation
	Photocatalysis	
	Hybrid systems	

a demand for processes based on renewable energy. The wide recognition of these issues inspired goal-oriented research. Inventions were made that could not have been foreseen but had considerable consequences.

In the second column the technologies are listed. We recognize several of these from the previous sections. It appears that very often the new catalytic technology relates to utilizing the discovery of a new catalytically active material or complex. These are listed in the final column.

Whereas heterogeneous catalysis gave rise to the construction of highly efficient large-scale processes, we see in our age a shift to smaller scales and also to the use of catalysis in various devices.

The automotive exhaust catalyst illustrates this. The reactor is embedded in the exhaust of the automotive engine and operates by integration with gas sensors and computer control. This trend persists in fuel cell development and devices for hydrogen storage and solar energy conversion.

1.3
Fundamental Catalysis in Practice

There are economic constraints on catalyst cost, catalytic performance, and process selection that are very relevant. Catalyst improvement does not necessarily lead to a practically relevant system. Interestingly, as the matter of catalyst choice will illustrate, there is a direct relationship between molecular predictive understanding and new options for catalyst choice. Catalytic performance and reactor choice are determined, among other things, by extrinsic kinetics, in which mass and heat transfer play a dominant role. In energy conversion technology, process selection of preferred conversion processes is largely determined by how the energy content of product and raw material relate.

1.4
Catalyst Selection

A major contribution of computational catalysis is the development of a computational approach to evaluating and predicting the catalytic activity of heterogeneous catalytic systems. This method uses the dependence of a measured rate of some reaction as a function of a reactivity descriptor that can be calculated. The method exploits the physical chemical interpretation of the volcano type behavior that is found in this way. This is a consequence of the Sabatier principle. If one uses the interaction strength of a reactant with a catalyst as a reactivity parameter the maximum in the volcano curve occurs where the rate of reactant activation and that of product desorption are the same (see Figure 1.2).

To the left of the volcano the rate of reaction increases with increasing interaction energy, to the right it decreases with increasing reaction energy. The overall catalytic rate shows a maximum rate at an optimum value of the reactivity descriptor.

The second ingredient in the extrapolative prediction of the rate is the use of a Brønsted type linear activation energy–reactivity descriptor relationship for elementary surface reactions. As reactivity descriptor a thermodynamic quantity as the reaction energy of an essential elementary reaction step is used. For surface reactions this is called the Brønsted–Evans–Polanyi relationship (BEP).

An example of such a relationship is shown in Figure 1.3a. The computed activation energy for CO dissociation, that is, for C–O bond cleavage, is plotted against the sum of the adsorption energies of adsorbed C and O. The surface structure is corrugated.

The slope of the curve, the BEP proportionality constant, is nearly one. It indicates that the structure of transition state and dissociated state are very similar and that in the transition state the C–O bond is very weak. Once the validity of the BEP relationship for an essential reaction step of a catalytic reaction step has been established the relevant descriptor can be used to construct a volcano curve when a large set of experimental data is available. One can also use microkinetic modeling techniques of the intrinsic catalytic rate to create such a data set computationally.

Figure 1.3b shows a plot of the experimentally measured rate constants of the catalytic reaction:

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

against a reactivity descriptor that is the sum of the adsorption energies of the dissociation products E_{diss}. A volcano-type reaction rate dependence is found in accordance with the Sabatier principle. The optimum value of the reactivity descriptor is close to 0.

Access to a volcano curve such as that in Figure 1.3b creates the possibility to computationally screen many metal combinations. One then has to calculate the sum of the adsorption energies of C and O (E_{diss}) for different metal compositions. In this way the reaction rate for many metal combinations can be computationally analyzed.

The method has been used to find alternatives to the expensive Co and Ru metals that show maximum performance for the methane reforming reaction. Figure 1.4 illustrates the way these data can be used to arrive at an economic decision as to which is the material to be preferred.

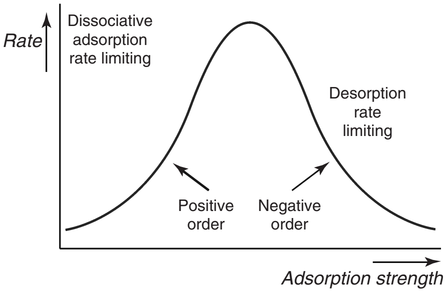

Figure 1.2 Sabatier's catalytic reactivity principle; rate reaches a maximum at optimum interaction strength of reagent and catalyst.

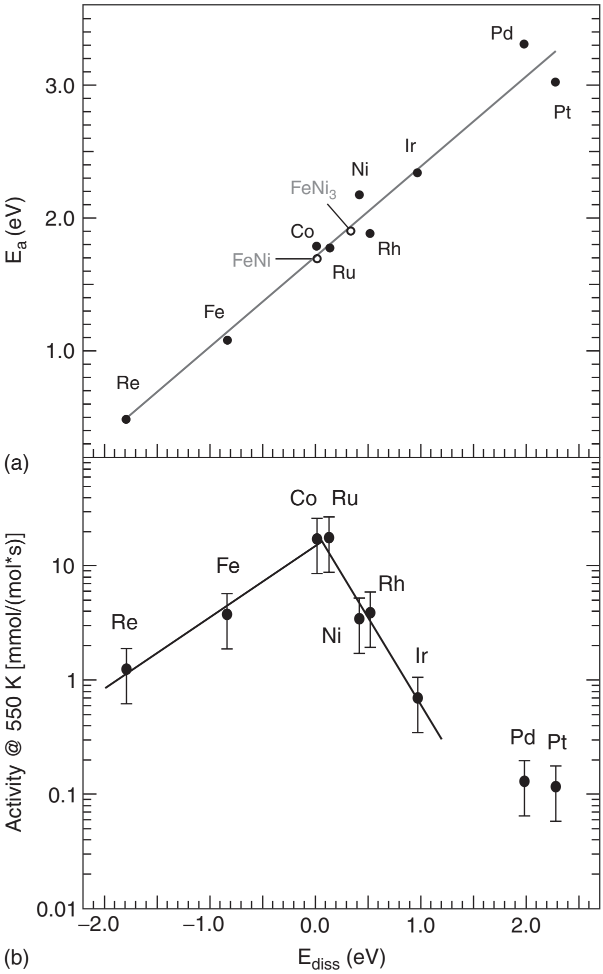

Figure 1.3 (a) BEP relationship for the activation energy for CO dissociation vs the CO dissociation energy, E_{diss}. (b) Measured catalytic activities for supported metal catalysts are shown vs E_{diss}. The calculations were performed using the RPBE exchange correlation on periodically repeated stepped fcc (211) metal slabs with 12 layers in the (211) direction (adapted from Ref. [2]).

Shown is a so-called Pareto plot of E_{diss} for a particular metal combination against the price of this combination. When ΔE_{diss} is zero the performance of the material is maximal. Only in exceptional cases will this coincide with the lowest price. The Pareto plot allows for a choice in which there is a trade-off between lowest process and best performance. According to the Pareto plot the lowest price with close to maximum performance is the alloy FeNi$_3$.

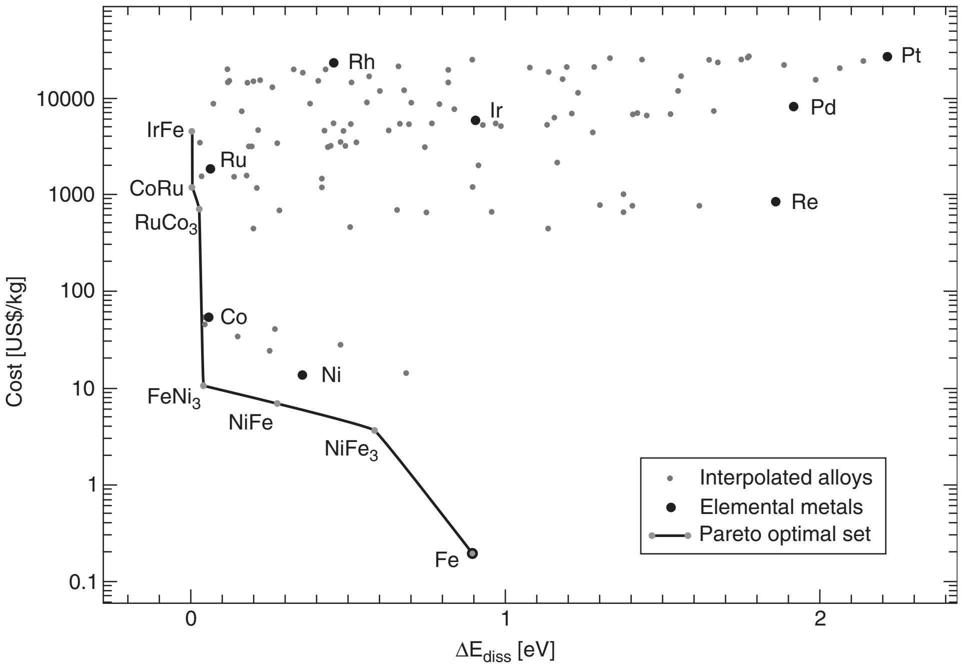

Figure 1.4 Pareto plot of the activity measure $\Delta E_{\text{diss}} = \left|E'_{\text{diss}} - E^{\text{opt}}_{\text{diss}}\right|$ and the cost for 117 elemental metals and bimetallic alloys (adapted from Ref. [2]).

1.5
Reactor Choice

The catalyst of maximum activity is not always the catalyst that is useful in practice. The overall rate of a catalytic reaction also depends on extrinsic kinetic parameters such as rates of mass and heat transfer. In Figure 1.5 reactivity regimes are compared for three processes. The petroleum geochemical processes generate the oil and gas reservoirs. The space–time yield of such processes is very low. There is also a comparison of biochemical processes for fermentation and the optimum process window for industrial catalysis. Note the three orders of

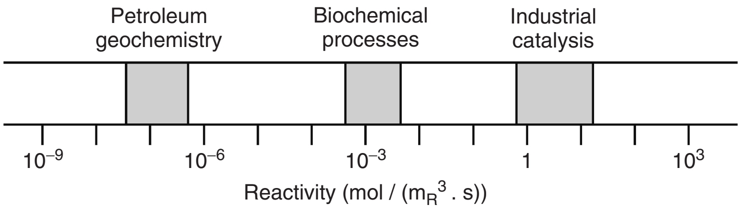

Figure 1.5 Reactivity regimes for different chemical processes.

magnitude difference between industrial catalysis and biochemical processes. The reason for the optimum window of the industrial process is the trade-off between two parameters. One is the intrinsic rate of a catalyst, which preferably is maximal. However, when the rate of a reaction becomes very high other factors can become limiting, such as the rate at which mass can be transported to or from the catalyst or the amount of heat to be supplied or removed.

Reactor design sets these limitations. The process is typically executed at the optimum condition where mass and heat transfer limit production rate. Intrinsic kinetics then sets the limiting values that can be used. Clearly the better the extrinsic kinetic parameters are controlled and can be increased, the higher the production.

1.6
Process Choice

The thermodynamic and material efficiency of a process are critical to its selection. A measure of material efficiency is the concept of Atom Utilization introduced by R. Sheldon [3]. The essential idea is to evaluate the production of waste material by simply counting the ratio of the number of atoms in the reactant material to the number of atoms in the product. For practical purposes it is useful to convert the Atom Utilization number into a weight ratio, so as to evaluate the efficiency on a weight basis.

The effective Atom Utilization can be influenced by the choice of catalyst and reactor. It depends on the selectivity of a reaction. We illustrate this for epoxidation processes to ethylene (Figure 1.6).

The classical route proceeds through the intermediate chlorohydrin using Cl_2 and $Ca(OH)_2$ as reactants. Atom Utilization is 25% with $CaCl_2$ as waste product. The catalytic process based on Ag ideally produces ethylene epoxide with 100% selectivity. The Atom Utilization is 100%. In practice the reaction is run with 90% selectivity giving an effective Atom Utilization of 77%. It illustrates the importance of catalytic processes. This number is still significantly higher than that of the chlorohydrin route.

In dealing with such transformation processes as the conversion of coal or gas to liquid fuels for transportation thermal efficiency is critically important. This is the heat of combustion of the products divided by that of (all) the feedstock used. For example, the thermal efficiency of oil refineries is typically 90%. This is to be contrasted to the thermal efficiency of the production of a non-fuel product such as methanol, which has a thermal efficiency of only 67%.

De Jong [4] mentions two important principles for efficient processes:

- minimizing the difference in hydrogen content between feed and product, and
- minimizing the number of process steps.

The importance of hydrogen content is illustrated by the conversion of natural gas or coal into liquid energy carriers. As illustrated in Figure 1.7, conversion

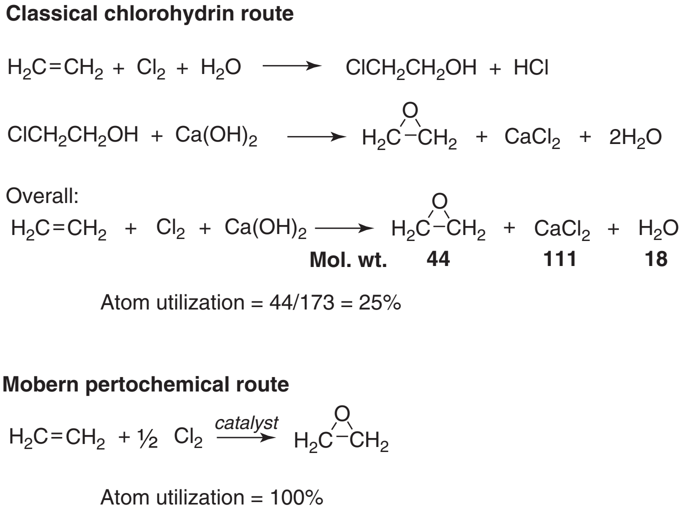

Figure 1.6 Atom utilization for the classical chlorohydrin route to ethylene oxide is 25%, whereas that of the modern petrochemical route is 100%.

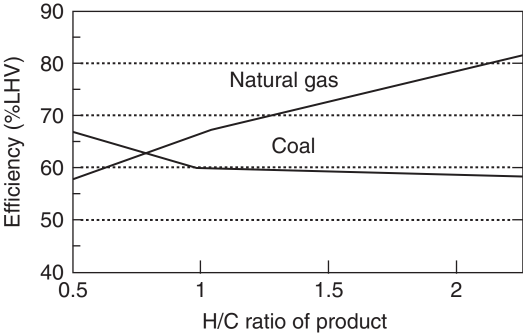

Figure 1.7 Maximum thermal efficiency for synthetic fuels: synthesis gas to hydrocarbons (reproduced from Ref. [4]).

of natural gas into hydrogen-rich paraffinic molecules has a substantially higher thermal efficiency than the conversion of coal.

Aromatic gasoline ($H/C = 1$) has a substantially lower thermal efficiency than paraffin ($H/C = 2$). There is a very low thermal efficiency of fuel production via the synthesis gas route because of the energy cost of coal gasification. Production of liquid fuels via direct hydrogen addition (Bergius process) is more efficient.

De Jong also gives an interesting example of the effect of the introduction of several process steps. The example is the production of methyl *tert*-butyl ether.

Direct etherification from isobutane requires one step, and reaction with *n*-butene requires an additional isomerization step, whereas reaction with butane needs an

Table 1.2 Energy use in MTBE manufacturing [4].

Process/feedstok[a]	Process/name	Energy consumed (GJ/t MTBE)[b]
$iso\text{-}C_4^{2-} + MeOH \rightarrow MTBE$	Etherification	<0.1
$n\text{-}C_4^{2-} + MeOH \rightarrow MTBE$	Isomerization	1.9
$iso\text{-}C_4^{0} + MeOH \rightarrow MTBE + H_2$	Dehydrogenation	5.5

[a] C_4^{2-} = butene, C_4^{0} = butane, and MeOH = methanol.
[b] Energy consumptions excluding low-pressure steam.

additional dehydrogenation step. Table 1.2 shows the increasing use of energy with number of process steps.

References

1. Reetz, M. and Jaeger, K.-E. (1999) Superior biocatalysts by directed evolution. *Biocatal. Discov. Appl.*, **200**, 31–57.
2. Andersson, M.P. *et al.* (2006) Toward computational screening in heterogeneous catalysis: pareto-optimal methanation catalysts. *J. Catal.*, **239** (2), 501–506.
3. Sheldon, R.A. (1994) Consider the environmental quotient. *Chemtech*, **24** (3), 38–47.
4. De Jong, K.P. (1996) Efficient catalytic processes for the manufacturing of high-quality transportation fuels. *Catal. Today*, **29** (1–4), 171–178.

Further Reading

Jencks, W. (1969) *Catalysis in Chemistry and Enzymology*, McGraw-Hill, New York.
Moulijn, J.A., Makkee, M., and van Diepen, A. (2001) *Chemical Process Technology*, Wiley-VCH Verlag GmbH, Chichester.
Santen, R.Av. and Neurock, M. (2006) *Molecular Heterogeneous Catalysis*, Wiley-VCH Verlag GmbH, Weinheim.
van Leeuwen, P.W.M. (2004) *Homogeneous Catalysis*, Kluwer Academic Publishers, Dordrecht.