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Concepts of Modern Catalysis and Kinetics

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Cover illustration
Artistic view of surface reaction and potential energy barriers. Painted by Ove Broo, reproduced with kind permission.

Library of Congress Card No.:
Applied for.

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by Die Deutsche Bibliothek
Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie, detailed bibliographic data is available in the Internet at <http://dnb.ddb.de>.

Printed in the Federal Republic of Germany
Printed on acid-free paper.

Composition Kühn & Weyh, Freiburg
Printing Strauss Offsetdruck, Mörlenbach
Bookbinding Litges & Dopf Buchbinderei GmbH, Heppenheim

ISBN 3-527-30574-2

To Ina and Camilla

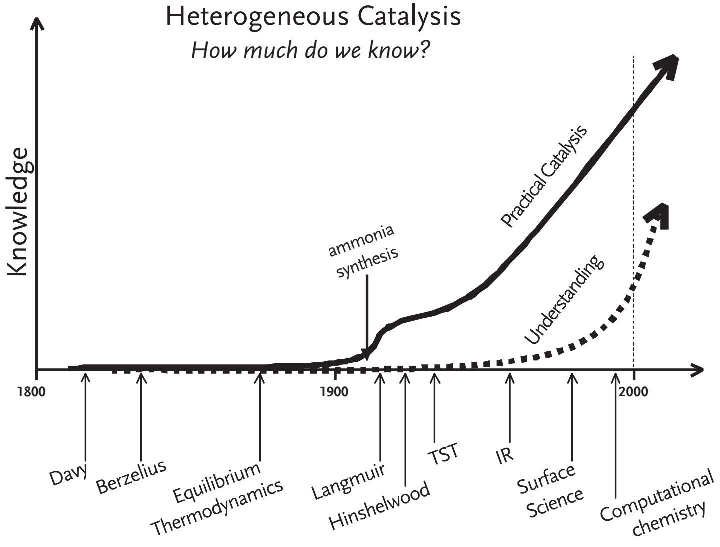
To Marianne, Hanneke,
Annemieke, Karin and Peter

Contents

Preface

Catalysis: conceptually understood but far away from maturity

Catalysis as a phenomenon is becoming reasonably well understood on a conceptual level. Recognized as a phenomenon and utilized around 1816 by Davy in the mine safety lamp, and defined around 1835 by Berzelius, catalysis obtained an extensive empirical basis by the systematic experiments of Mittasch in the early 20th century. Studies of catalytic mechanisms became feasible when Langmuir – Hinshelwood kinetics became available in the mid 1920s. Since then, for many decades fundamental catalysis became more or less synonymous with kinetic analysis. The advent of spectroscopy, starting with infrared spectroscopy in the late 1950s, followed by a range of other techniques for catalyst characterization and investigation of surface species opened the opportunity to relate catalytic properties with composition and structure of materials. Surface science enabled one to resolve adsorption geometries and reactivity patterns in well-defined structures, culminating in scanning tunneling spectroscopy as the ultimate tool to resolve surface structure and adsorbed spe-



cies with atomic precision by the end of the 20th century. Techniques have become available to study catalysts under working conditions. Ever increasing computational power enables the calculation of adsorbate geometries, bond strengths and even reaction rates. Anno 2003, catalysis has developed into a scientific discipline with a firm conceptual basis. The relation between catalytic activity for a certain reaction and the composition, structure of a surface is in general qualitatively well understood, provided the surfaces are relatively simple and defined.

However, the prospect of designing a catalyst from first principles behind our desk is still far away. A number of reasons is responsible. Although we may be able to describe a catalytic reaction on a well-defined single crystal of a metal under well-defined and simplified conditions, this becomes tremendously more complicated when the same reaction runs over small catalyst particles on a support in a realistic reactor environment. The world of the ideal surface science laboratory and that of industrial practice are not only separated by the often cited pressure gap, but also by structural, and materials gaps. The complexity of small, supported crystallites that dynamically respond to every change in reaction environment is only beginning to be explored. Secondly, the way we describe the kinetics of catalytic reactions is, albeit greatly refined, still based on the adsorption isotherm of Langmuir (1915) and the kinetic formalism of Hinshelwood (1927), based on ideal surfaces with equivalent adsorption sites and adsorbate species that are randomly mixed and do not interact. This represents another gross over simplification, which has recently become recognized and is beginning to become addressed in terms of ensembles with reactivities many orders of magnitude more reactive than the planar surfaces.

This book intends to be an introduction to the fundamentals of heterogeneous catalysis, aiming to explain the phenomenon of catalysis on a conceptual level. Kinetics, being the tool to investigate and describe catalytic reactivity as it expresses itself in a reactor, plays an important role in this book. Also reaction rate theory, providing the formalism to relate reaction rates to molecular structure of reacting species is described extensively. Next we describe catalytic surfaces, as well as the tools to study them. With this knowledge we treat surface reactivity in greatly simplified molecular orbital theory, again with the aim to give a conceptual explanation of how a catalyst works and what are the trends when going from one surface/structure to another. The final chapters serve to illustrate catalysis in practice, to give the reader an impression of how catalysis is applied. We emphasize that the book is a textbook, written for students in chemistry, physics and chemical engineering who are interested in understanding the concepts. Many more important details are worthwhile knowing, but are beyond the scope of this book and will have to be found in specialist literature.

This book is based on courses, which the authors have taught at Lyngby and Eindhoven for many years. For example, Chapters 1–3 form the basis for a mandatory course “Kinetics and Catalysis” presented in the second year of the Bachelor’s curriculum at Eindhoven, while Chapters 4,5 and 8–10 formed the basis for an optional course Introduction to Catalysis. In Lyngby, Chapters 1–7 have been used for an optional course in “Chemical Reaction Kinetics and Catalysis” in the Master’s curriculum. At the end of the book we have added a list of questions for every chapter, which students may use to test their knowledge. The exercises are mainly meant to enable students to acquire skills in kinetic modelling. Some of these exercises have been used in written examinations. We intend to make solutions available on our web sites (www.icat.dtu.dk and www.catalysis.nl).

The authors are indebted to many colleagues in the field of catalysis and surface science. We mention in particular Jens Nørskov and Rutger van Santen. Both made very substantial contributions to the theory of heterogeneous catalysis. We are very grateful for the many extensive and pleasant discussions we had with them. Also our contacts with industry have been most inspiring and indispensable. We mention in particular Haldor Topsøe A/S in Lyngby and the Shell Research and Technology Centre in Amsterdam. We also want to thank the numerous students who followed our courses in Lyngby and Eindhoven. They have taught us more than they perhaps realize. Finally we thank our families who patiently allowed us to spend a considerable amount of time on this book. We devote this book to them.

Lyngby/Eindhoven
June 2003

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1
Introduction to Catalysis

Ask the average person in the street what a catalyst is, and he or she will probably tell you that a catalyst is what one has under the car to clean up the exhaust. Indeed, the automotive exhaust converter represents a very successful application of catalysis; it does a great job in removing most of the pollutants from the exhaust leaving the engines of cars. However, catalysis has a much wider scope of application than abating pollution.

Catalysis in Industry

Catalysts are the workhorses of chemical transformations in the industry. Approximately 85–90 % of the products of chemical industry are made in catalytic processes. Catalysts are indispensable in

- Production of transportation fuels in one of the approximately 440 oil refineries all over the world
- Production of bulk and fine chemicals in all branches of chemical industry
- Prevention of pollution by avoiding formation of waste (unwanted byproducts)
- Abatement of pollution in end-of-pipe solutions (automotive and industrial exhaust)

A catalyst offers an alternative, energetically favorable mechanism to the non-catalytic reaction, thus enabling processes to be carried out under industrially feasible conditions of pressure and temperature.

For example, living matter relies on enzymes, which are the most specific catalysts one can think of. Also, the chemical industry cannot exist without catalysis, which is an indispensable tool in the production of bulk chemicals, fine chemicals and fuels.

For scientists and engineers catalysis is a tremendously challenging, highly multidisciplinary field. Let us first see what catalysis is, and then why it is so important for mankind.

1.1
What is Catalysis?

A catalyst accelerates a chemical reaction. It does so by forming bonds with the reacting molecules, and by allowing these to react to a product, which detaches from the catalyst, and leaves it unaltered such that it is available for the next reaction. In fact, we can describe the catalytic reaction as a cyclic event in which the catalyst participates and is recovered in its original form at the end of the cycle.

Let us consider the catalytic reaction between two molecules A and B to give a product P, see Fig. 1.1. The cycle starts with the bonding of molecules A and B to the catalyst. A and B then react within this complex to give a product P, which is also bound to the catalyst. In the final step, P separates from the catalyst, thus leaving the reaction cycle in its original state.

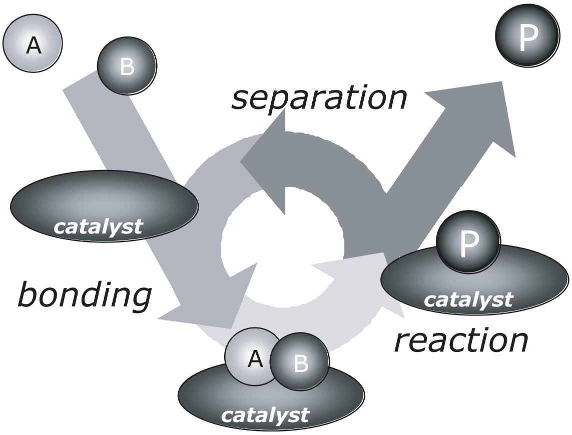

Figure 1.1. Every catalytic reaction is a sequence of elementary steps, in which reactant molecules bind to the catalyst, where they react, after which the product detaches from the catalyst, liberating the latter for the next cycle.

To see how the catalyst accelerates the reaction, we need to look at the potential energy diagram in Fig. 1.2, which compares the non-catalytic and the catalytic reaction. For the non-catalytic reaction, the figure is simply the familiar way to visualize the Arrhenius equation: the reaction proceeds when A and B collide with sufficient energy to overcome the activation barrier in Fig. 1.2. The change in Gibbs free energy between the reactants, A + B, and the product P is ΔG.

The catalytic reaction starts by bonding of the reactants A and B to the catalyst, in a spontaneous reaction. Hence, the formation of this complex is exothermic, and the free energy is lowered. There then follows the reaction between A and B while they are bound to the catalyst. This step is associated with an activation energy; however, it is significantly lower than that for the uncatalyzed reaction. Finally, the product P separates from the catalyst in an endothermic step.

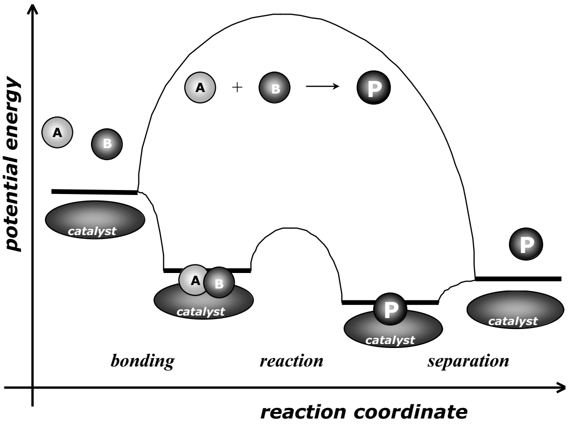

Figure 1.2. Potential energy diagram of a heterogeneous catalytic reaction, with gaseous reactants and products and a solid catalyst. Note that the uncatalyzed reaction has to overcome a substantial energy barrier, whereas the barriers in the catalytic route are much lower.

The energy diagram of Fig. 1.2 illustrates several important points:

- The catalyst offers an alternative path for the reaction, which is obviously more complex, but energetically much more favorable.
- The activation energy of the catalytic reaction is significantly smaller than that of the uncatalyzed reaction; hence, the rate of the catalytic reaction is much larger (we explain this in greater detail in Chapter 2).
- The overall change in free energy for the catalytic reaction equals that of the uncatalyzed reaction. Hence, the catalyst does not affect the equilibrium constant for the overall reaction of A + B to P. Thus, if a reaction is thermodynamically unfavorable, a catalyst cannot change this situation. A catalyst changes the kinetics but *not* the thermodynamics.
- The catalyst accelerates both the forward and the reverse reaction to the same extent. In other words, if a catalyst accelerates the formation of the product P from A and B, it will do the same for the decomposition of P into A and B.

Thus far it is immediately evident that there are also cases in which the combination of catalyst with reactants or products will not be successful:

- If the bonding between reactants and catalyst is too weak, there will be hardly any conversion of A and B into products.
- Conversely if the bond between the catalyst and one of the reactants, say A, is too strong, the catalyst will be mostly occupied with species A, and B is not available to form the product. If A and B both form strong bonds with the catalyst, the intermediate situation with A or B on the catalyst may be so stable that

reaction becomes unlikely. In terms of Fig. 1.2, the second level lies so deep that the activation energy to form P on the catalyst becomes too high. The catalyst is said to be poisoned by (one of) the reactants.

- In the same way, the product P may be too strongly bound to the catalyst for separation to occur. In this case the product poisons the catalyst.

Hence, we intuitively feel that the successful combination of catalyst and reaction is that in which the interaction between catalyst and reacting species is not too weak, but also not too strong. This is a loosely formulated version of Sabatier's Principle, which we encounter in a more precise form in Chapter 2 and in detail in Section 6.5.3.5.

Until now, the catalyst has been an unspecified, abstract body, so let us first look at what kind of catalysts exist.

1.2
Catalysts Can Be Atoms, Molecules, Enzymes and Solid Surfaces

Catalysts come in a multitude of forms, varying from atoms and molecules to large structures such as zeolites or enzymes. In addition they may be employed in various surroundings: in liquids, gases or at the surface of solids. Preparing a catalyst in the optimum form and studying its precise composition and shape are an important specialism, which we describe in later chapters.

It is customary to distinguish the following three subdisciplines in catalysis: homogeneous, heterogeneous and bio catalysis. We illustrate each with an example.

1.2.1
Homogeneous Catalysis

In homogeneous catalysis, both the catalyst and the reactants are in the same phase, i.e. all are molecules in the gas phase, or, more commonly, in the liquid phase. One of the simplest examples is found in atmospheric chemistry. Ozone in the atmosphere decomposes, among other routes, via a reaction with chlorine atoms:

$$\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO_3}$$
$$\mathrm{ClO_3} \rightarrow \mathrm{ClO} + \mathrm{O_2}$$
$$\mathrm{ClO} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{O_2}$$

or overall

$$\mathrm{O_3} + \mathrm{O} \rightarrow 2\mathrm{O_2}$$

Ozone can decompose spontaneously, and also under the influence of light, but a Cl atom accelerates the reaction tremendously. As it leaves the reaction cycle unaltered, the Cl atom is a catalyst. Because both reactant and catalyst are both in the same phase, namely the gas phase, the reaction cycle is an example of homogeneous catalysis. (This reaction was historically important in the prediction of the ozone hole.)

Industry uses a multitude of homogenous catalysts in all kinds of reactions to produce chemicals. The catalytic carbonylation of methanol to acetic acid

$$CH_3OH + CO \rightarrow CH_3COOH$$

by $[Rh(CO)_2I_2]^-$ complexes in solution is one of many examples. In homogeneous catalysis, often aimed at the production of delicate pharmaceuticals, organometallic complexes are synthesized in procedures employing molecular control, such that the judicious choice of ligands directs the reacting molecules to the desired products.

1.2.2
Biocatalysis

Enzymes are nature's catalysts. For the moment it is sufficient to consider an enzyme as a large protein, the structure of which results in a very shape-specific active site (Fig. 1.3). Having shapes that are optimally suited to guide reactant molecules (usually referred to as substrates) in the optimum configuration for reaction, enzymes are highly specific and efficient catalysts. For example, the enzyme catalase catalyzes the decomposition of hydrogen peroxide into water and oxygen

$$2H_2O_2 \xrightarrow[\text{catalase}]{} H_2O + O_2$$

at an incredibly high rate of up to 10^7 hydrogen peroxide molecules per second!

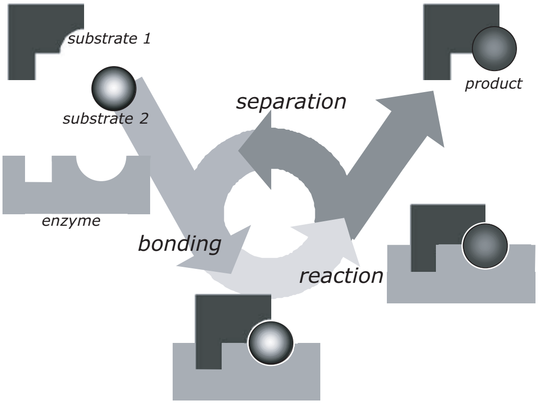

Figure 1.3. Schematic representation of an enzyme-catalyzed reaction. Enzymes often match the shape of the substrates they bind to, or the transition state of the reaction they catalyze. Enzymes are highly efficient catalysts and represent a great source of inspiration for designing technical catalysts.

Enzymes allow biological reactions to occur at the rates necessary to maintain life, such as the build up of proteins and DNA, or the breakdown of molecules and the storage of energy in sugars. An example with, perhaps, some special appeal to students is the breakdown of alcohol to acetaldehyde inside the body by the enzyme alcohol dehydrogenase. The acetaldehyde in turn is converted into acetate by aldehyde hydrogenase. Some people cannot tolerate alcohol (as revealed by facial flushing after drinking a small amount) because they lack the form of the enzyme that breaks down acetaldehyde.

1.2.3
Heterogeneous Catalysis

In heterogeneous catalysis, solids catalyze reactions of molecules in gas or solution. As solids – unless they are porous – are commonly impenetrable, catalytic reactions occur at the surface. To use the often expensive materials (e.g. platinum) in an economical way, catalysts are usually nanometer-sized particles, supported on an inert, porous structure (see Fig. 1.4). Heterogeneous catalysts are the workhorses of the chemical and petrochemical industry and we will discuss many applications of heterogeneous catalysis throughout this book.

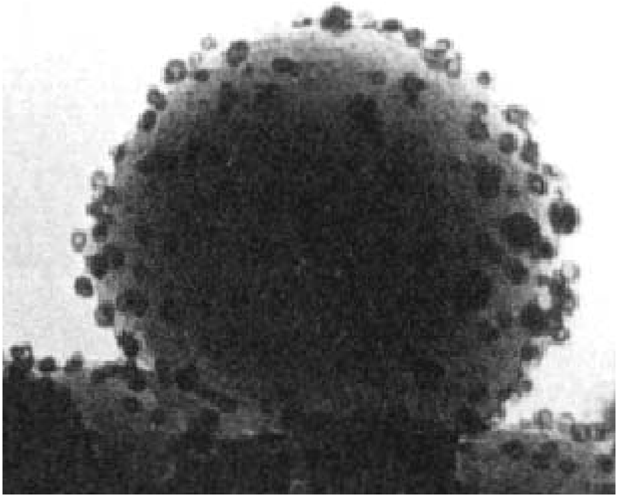

Figure 1.4. Catalysts are nanomaterials and catalysis is nanotechnology. If we define nanotechnology as the branch of materials science aiming to control material properties on the nanometer scale, then catalysis represents a field where nanomaterials have been applied commercially for about a century. Many synthetic techniques are available to produce small particles for heterogeneous catalysts, and to keep them sufficiently stable so that they can withstand the often hostile conditions of an industrial reactor. Modern catalysis is preeminently nanotechnology. [Figure adapted from A.K. Datye and N.J. Long, *Ultramicroscopy* **25** (1988) 203.]

As an introductory example we take one of the key reactions in cleaning automotive exhaust, the catalytic oxidation of CO on the surface of noble metals such as platinum, palladium and rhodium. To describe the process, we will assume that the metal surface consists of active sites, denoted as "$*$." We define them properly later on. The catalytic reaction cycle begins with the adsorption of CO and O_2 on the surface of platinum, whereby the O_2 molecule dissociates into two O atoms (X^* indicates that the atom or molecule is adsorbed on the surface, i.e. bound to the site $*$):

$$O_2 + 2^* \rightleftharpoons 2O^*$$
$$CO+^* \rightleftharpoons CO^*$$

The adsorbed O atom and the adsorbed CO molecule then react on the surface to form CO_2, which, being very stable and relatively unreactive, interacts only weakly with the platinum surface and desorbs almost instantaneously:

$$CO^* + O^* \rightleftarrows CO_2 + 2^*$$

Note that in the latter step the adsorption sites on the catalyst are liberated, so that these become available for further reaction cycles. Figure 1.5 shows the reaction cycle along with a potential energy diagram.

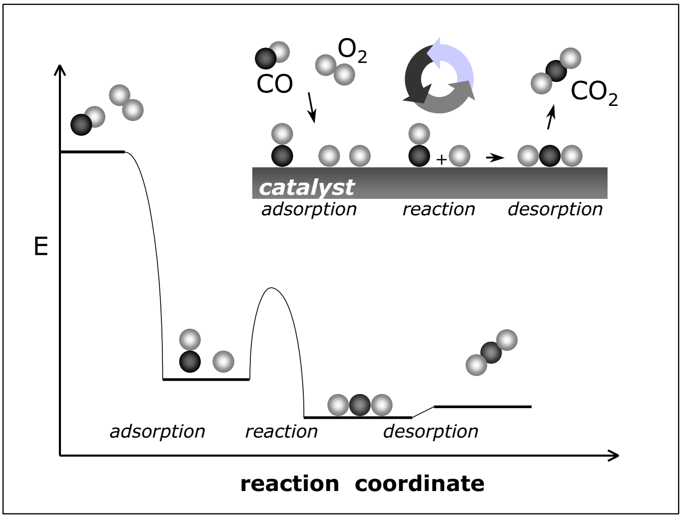

Figure 1.5. Reaction cycle and potential energy diagram for the catalytic oxidation of CO by O_2.

Where in this cycle is the essential influence of the catalyst? Suppose we carry out the reaction in the gas phase without a catalyst. The reaction will proceed if we raise the temperature sufficiently for the O_2 molecule to dissociate into two O atoms (radicals). Once these radicals are available, the reaction with CO to CO_2 follows instantaneously.

The activation energy of the gas phase reaction will be roughly equal to the energy required to split the strong O–O bond in O_2, i.e. about 500 kJ mol^{-1}. In the catalytic reaction, however, the O_2 molecule dissociates easily – in fact without an activation energy – on the surface of the catalyst. The activation energy is associated with the reaction between adsorbed CO and O atoms, which is of the order of 50–100 kJ mol^{-1}. Desorption of the product molecule CO_2 costs only about 15–30 kJ mol^{-1} (depending on the metal and its surface structure). Hence if we compare the catalytic and the uncatalyzed reaction, we see that the most difficult step of the homogeneous gas phase reaction, namely the breaking of the O–O bond is easily performed by the catalyst. Consequently, the ease with which the CO_2 molecule forms determines the rate at which the overall reaction from CO and O_2 to CO_2 proceeds. This is a very general situation for catalyzed reactions, hence the expression: A catalyst breaks bonds, and lets other bonds form. The beneficial action of the catalyst is in the dissociation of a strong bond, the subsequent steps might actually proceed faster without the catalyst (which is a hypothetical situation of course). In Chapter 6 we analyze in detail how a surface induces the breaking of intramolecular bonds.

1.3
Why is Catalysis Important?

The chemical industry of the 20th century could not have developed to its present status on the basis of non-catalytic, stoichiometric reactions alone. Reactions can in general be controlled on the basis of temperature, concentration, pressure and contact time. Raising the temperature and pressure will enable stoichiometric reactions to proceed at a reasonable rate of production, but the reactors in which such conditions can be safely maintained become progressively more expensive and difficult to make. In addition, there are thermodynamic limitations to the conditions under which products can be formed, e.g. the conversion of N_2 and H_2 into ammonia is practically impossible above 600 °C. Nevertheless, higher temperatures are needed to break the very strong $N\equiv N$ bond in N_2. Without catalysts, many reactions that are common in the chemical industry would not be possible, and many other processes would not be economical.

Catalysts accelerate reactions by orders of magnitude, enabling them to be carried out under the most favorable thermodynamic regime, and at much lower temperatures and pressures. In this way efficient catalysts, in combination with optimized reactor and total plant design, are the key factor in reducing both the investment and operation costs of a chemical processes. But that is not all.

1.3.1
Catalysis and Green Chemistry

Technology is called “green” if it uses raw materials efficiently, such that the use of toxic and hazardous reagents and solvents can be avoided while formation of waste or undesirable byproducts is minimized. Catalytic routes often satisfy these criteria.

A good example is provided by the selective oxidation of ethylene to ethylene epoxide, an important intermediate towards ethylene glycol (antifreeze) and various polyethers and polyurethanes (Fig. 1.6).

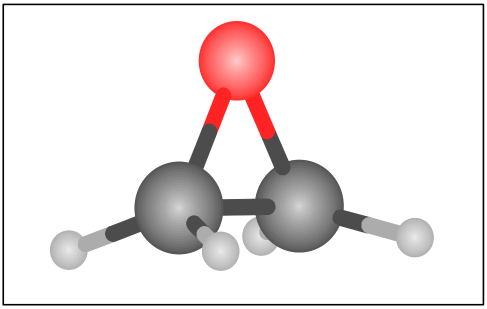

Figure 1.6. Ethylene epoxide, an important intermediate in the chemical industry.

The old, non-catalytic route (called the epichlorohydrine process) follows a three-step synthesis:

$$Cl_2 + NaOH \rightarrow HOCl + NaCl \tag{1}$$

$$C_2H_4 + HOCl \rightarrow CH_2Cl\text{–}CH_2OH \quad \text{(epichlorohydrine)} \tag{2}$$

$$CH_2Cl\text{–}CH_2OH + {}^1\!/_2Ca(OH)_2 \rightarrow {}^1\!/_2CaCl_2 + C_2H_4O + H_2O \tag{3}$$

or in total:

$$Cl_2 + NaOH + {}^1\!/_2Ca(OH)_2 + C_2H_4 \rightarrow C_2H_4O + {}^1\!/_2CaCl_2 + NaCl + H_2O$$

Hence, for every molecule of ethylene oxide, 1 molecule of salt is formed, creating a waste problem that was traditionally solved by dumping it in a river. Such practice is of course now totally unacceptable.

The catalytic route, however, is simple and clean, although it does produce a small amount of CO_2. Using silver, promoted by small amounts of chlorine, as the catalyst, ethylene oxide is formed directly from C_2H_4 and O_2 at a selectivity of around 90%, with about 10% of the ethylene ending up as CO_2. Nowadays all production facilities for ethylene oxide use catalysts.

1.3.2
Atom Efficiency, *E* Factors and Environmental Friendliness

Numerous organic syntheses are based on stoichiometric oxidations of hydrocarbons with sodium dichromate and potassium permanganate, or on hydrogenations with alkali metals, borohydrides or metallic zinc. In addition, there are reactions such as aromatic nitrations with H_2SO_4 and HNO_3, or acylations with $AlCl_3$ that generate significant amounts of inorganic salts as byproducts.

Fine chemicals are predominantly (but not exclusively!) the domain of homogeneous catalysis, where solvents present another issue of environmental concern. According to Sheldon, the best solvent is no solvent, but if a solvent is unavoidable, then water is a good candidate. [R.A. Sheldon, *J. Chem. Tech. Biotechnol.* **68** (1997) 381].

Sheldon has introduced several indicators to measure the efficiency and environmental impact of a reaction. The atom efficiency is the molecular weight of the desired product divided by the total molecular weight of all products. For example the conventional oxidation of a secondary alcohol

$$3C_6H_5\text{–}CHOH\text{–}CH_3 + 2CrO_3 + 3H_2SO_4 \rightarrow 3C_6H_5\text{–}CO\text{–}CH_3 + Cr_2(SO_4)_3 + 6H_2O$$

has an atom efficiency of 360/860 = 42 %. By contrast, the catalytic route

$$C_6H_5\text{–}CHOH\text{–}CH_3 + {}^1\!/_2O_2 \rightarrow C_6H_5\text{–}CO\text{–}CH_3 + H_2O$$

offers an atom efficiency of 120/138 = 87 %, with water as the only byproduct. The reverse step, a catalytic hydrogenation, proceeds with 100 % atom efficiency:

$$C_6H_5\text{–}CO\text{–}CH_3 + H_2 \rightarrow C_6H_5\text{–}CHOH\text{–}CH_3$$

as does the catalytic carbonylation of this molecule:

$$C_6H_5\text{–}CHOH\text{–}CH_3 + CO \rightarrow C_6H_5\text{–}CH(CH_3)COOH$$

Another useful indicator of environmental acceptability is the *E* factor – the weight of waste or undesirable byproduct divided by the weight of the desired product. As Tab. 1.1 shows, the production of fine chemicals and pharmaceuticals generate the highest amounts of waste per unit weight of product. Atom efficiencies and *E* factors can be calculated from each other, but in practice *E* factors can be higher due to yields being less than optimum and reagents that are used in excess. Also, loss of solvents should be included, and perhaps even the energy consumption with the associated generation of waste CO_2.

Table 1.1. Environmental acceptability of products in different segments of the chemical industry (from R.A. Sheldon, *Chem. Ind.* (1997) 12 and (1992) 903).

Industry segment	Product tonnage	*E* factor kg waste/kg product
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1 – 5
Fine chemicals	10^2–10^4	5–50
Pharmaceuticals	10–10^3	25–>100