Handbook of Catalysis

Chapter 1: Fundamentals of Catalysis

1.1. Introduction

When asked what a catalyst is, the average person on the street would likely say that it is what is inserted underneath the car to unsoil the exhaust. Certainly, the automotive exhaust converter is a very successful use of catalysis; it successfully eliminates the bulk of pollutants from vehicle engine exhaust. However, catalysis has a far larger use than pollution control (Roduner, 2018).

For instance, living organisms depend on enzymes, which are the most precise catalysts known to humankind. Furthermore, the chemical sector would not survive without catalysis, which is a critical instrument in the manufacturing of bulk chemicals, fuels, and fine chemicals (Ranocchiari and Bokhoven, 2011).

Catalysis is an extremely difficult and multidisciplinary field of study for scientists and engineers. To begin, let us define catalysis and then describe why it is vital to mankind (Armor, 1992).

1.2. What Is Catalysis?

A catalyst is a material that speeds up the pace of a chemical reaction. This is accomplished by forming bonds with the reactive molecules and allowing them to react, resulting in the formation of a product that separates from the catalyst, leaving it unaltered and ready for the next reaction. Indeed, the catalytic reaction may be thought of as a cyclic event in which the catalyst participates and is restored to its initial condition at the cycle's completion (Armor, 1992).

Consider the catalytic reaction that occurs between two molecules A and B, resulting in the product P. (see Figure. 1.1). When bonds form between molecules (i.e., A and B) and the catalyst, the cycle begins (Erkkilä et al., 2007). Then, within this complex, A and B react to produce P, which is likewise linked to the catalyst. P then separates from the catalyst, resuming the chemical cycle's initial condition (Watson and Parshall, 1985).
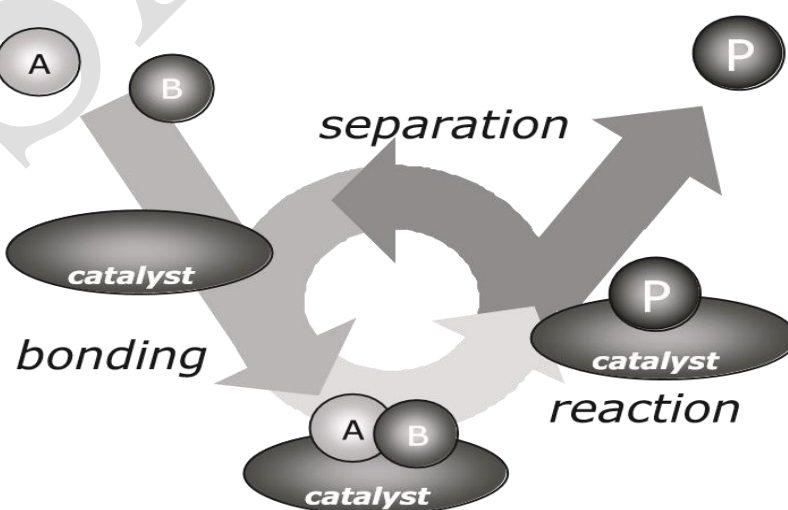
To understand how the catalyst speeds up the reaction, we must first look at the potential energy graph as shown in Figure 1.2, which contrasts non-catalytic and catalytic processes. The figure depicts the Arrhenius equation for the non-catalytic reaction in a familiar manner: the reaction occurs when A and B meet with enough energy to surpass the activation barrier in Figure 1.2. Differential of Gibbs free energy among the reactants (i.e., A + B) and the product (i.e., P) is denoted by the symbol DG (Ho, 1988).

The catalytic process begins when the reactants spontaneously bind to the catalyst. As a result, the process of creating this compound is exothermic, lowering the free level of energy. Then, while coupled to the catalyst, A and B react (Seiser et al., 2011). Although there is an activation energy in this phase, it is much lower than in the uncatalyzed process. Finally, the catalyst is separated from the product P by the endothermic process.
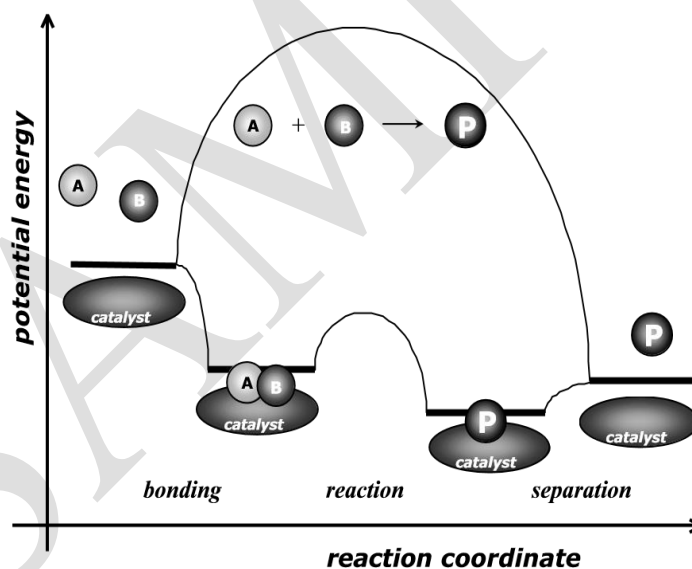

Figure 1.2. *Diagram depicting the potential energy of a heterogeneous catalytic process with products and reactants in gaseous form along with a solid catalyst.*
Note that the uncatalyzed process must overcome a significant energy barrier, while the catalytic pathway has significantly lower hurdles.
Source: https://application.wiley-vch.de/books/sample/3527316728_c01.pdf.

The following are significant properties of catalysts and catalysis (Hattori, 1995):

- The catalyst creates an additional reaction route that is obviously more difficult but substantially more energy-efficient.
- Because the catalytic process has a lot lower activation energy than the uncatalyzed reaction, the catalytic reaction advances at a much quicker rate.
- The overall variation in the free energy of the catalytic reaction is equal to the total variation in the free energy of the uncatalyzed process. As a consequence, the catalyst has no influence on the total A + B to P reaction's equilibrium constant. Thus, if the thermodynamics of a process are unfavorable, a catalyst will have no influence on the result. Catalysts affect the kinetics of a process but not its thermodynamics.
- The catalyst speeds both forward and reverse reactions greatly. In other words, if a catalyst accelerates the formation of P from A and B, it also accelerates P's decomposition into A and B.

Thus far, it is self-evident that the combination of catalyst and reactants or products will fail in several instances (Beletskaya et al., 2018):

- If the reaction between the reactants and the catalyst is insufficiently strong, just a little amount of A and B will be transformed to products.
- On the other hand, if the catalyst's affinity for one of the reactants, say A, is excessively great, the catalyst will be mostly filled by species A, leaving no space for the synthesis of the product. If both A and B form strong bonds with the catalyst, the intermediate state containing either A or B may become very stable, rendering the reaction implausible. According to Figure 1.2, the second level is so deep that the activation energy needed to generate P on the catalyst becomes too large. The catalyst, it is suggested, has been poisoned by (one of the) reactants.

Similarly, the product P may be too closely associated with the catalyst to permit separation. The product serves as a poison to the catalyst in this case.

Thus, we intuitively feel that an efficient catalyst-reaction combination is one in which the catalyst-reacting species interaction is neither too weak nor too strong. This is a condensed version of Sabatier's Principle.

Given that the catalyst has so far been a nameless, abstract material, let us first look at the many forms of catalysts (Armor, 2011).

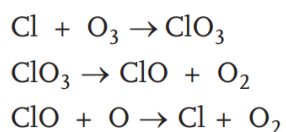## 1.3. Molecules, Atoms, Solid Surfaces, and Enzymes as Catalysts

Catalysts come in a range of forms and sizes, from atoms and molecules to bigger structures such as zeolites and enzymes. Additionally, they are applicable in a number of settings, including liquids, gasses, and at the surfaces of solids. Developing the best condition of a catalyst and investigating its

precise composition and form is a crucial specialty that we shall address in coming chapters (Marsh and Warburton, 1970).

Catalysis is often classified into three subfields: homogeneous, heterogeneous, and biocatalysis. Each is illustrated with a case study.

1.3.1. Homogeneous Catalysis

All molecules in homogeneous catalysis are in the same phase, whether it is the gas phase or the liquid phase (which occurs more often). One of the most straightforward examples may be found in the field of atmospheric chemistry. A variety of mechanisms exist in the atmosphere for ozone decomposition, one of which is interaction with chlorine atoms (Centi et al., 2002).

$$Cl + O_3 \rightarrow ClO_3$$
$$ClO_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

or overall:

$$O_3 + O \rightarrow 2O_2$$
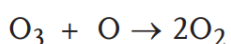
Ozone naturally decomposes and also under the influence of light, while the addition of a Cl atom significantly accelerates the process. Because the Cl atom has no effect on the chemical cycle, it functions as a catalyst. The reaction cycle demonstrates homogeneous catalysis since both reactants and catalysts are in the same phase, i.e., the gas phase. (In the past, this reaction was critical in anticipating the ozone hole (Panov et al., 1998).

In a range of chemical processes, industry use a variety of homogeneous catalysts. $[Rh(CO)_2I2]^-$ complexes in solution catalyze the methanol to acetic acid carbonylation, which is a good example of catalytic carbonylation.

$$CO + CH_3OH = CH_3COOH$$
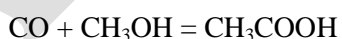
Homogeneous catalysis, which is widely employed to synthesize sensitive pharmaceuticals, results in the formation of organometallic complexes under molecular control, with the ligands steering the reactions toward the preferred products (Boltes et al., 2001).

1.3.2. Biocatalysis

Nature's catalysts are enzymes. For the time being, consider an enzyme to be a large protein with a highly specialized active site structure (Figure 1.3). Because enzymes' geometries are optimized for directing reactant molecules (commonly referred to as substrates) into the right configuration for reaction, they are exceptionally selective and efficient catalysts. For example, catalase catalyzes the breakdown of hydrogen peroxide into water and oxygen at an amazing rate of up to 107 molecules of hydrogen peroxide (H_2O_2) per second (Fu et al., 2010).

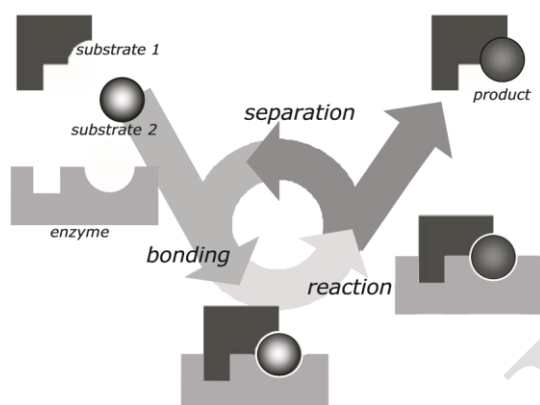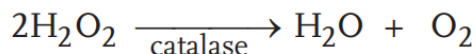$$2H_2O_2 \xrightarrow[\text{catalase}]{} H_2O + O_2$$

Figure 1.3. *An enzyme-catalyzed reaction is depicted schematically. Enzymes frequently conform to the geometry of their substrates or the transition state of the process that they catalyze. Enzymes are extremely efficient catalysts and provide a wealth of inspiration for the development of technological catalysts.*
Source: https://application.wiley-vch.de/books/sample/3527316728_c01.pdf.

Enzymes allow biological processes to occur at the rates necessary for life to exist, such as protein and DNA synthesis or chemical breakdown and energy storage in carbohydrates. A particularly intriguing example for children may be the body's alcohol dehydrogenase enzyme's breakdown of alcohol to acetaldehyde. The acetaldehyde is subsequently converted to acetate by aldehyde hydrogenase. Certain people are unable to handle alcohol (as demonstrated by facial flushing after a little quantity) due to a lack of the enzyme responsible for acetaldehyde degradation (Kawasaki et al., 2002).

1.3.3. Heterogeneous Catalysis

During heterogeneous catalysis, solids catalyze reactions involving molecules in gaseous or solution form. Because solids—with the exception of porous ones – are often impermeable, catalytic reactions occur near the surface. Catalysts are generally nanometer-sized particles supported on an inert and porous framework to maximize the use of commonly costly materials (e.g., platinum). Heterogeneous catalysts are often regarded as the workhorses of the petrochemical and chemical industries, and we will cover a range of heterogeneous catalysis applications throughout this book (Figure 1.4) (Sherwood et al., 2003).
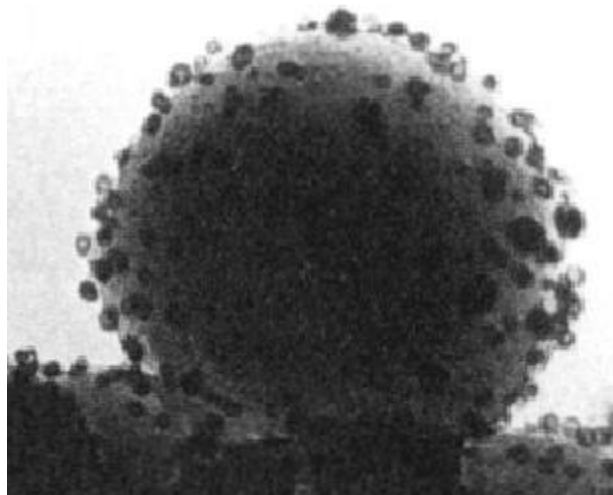
Figure 1.4. *The structure of a nanosized catalyst.*
Source: https://application.wiley-vch.de/books/sample/3527316728_c01.pdf.

As a starting point, consider one of the most important processes in automobile exhaust cleaning: the catalytic oxidation of carbon monoxide on the surface of inert metals such as platinum, palladium (Pd), and rhodium (Rh). Let us suppose that the metal surface has active sites, which are symbolized by the symbol "*," in order to better comprehend the process. Later on, they will be given the right classification. Initially, the adsorption of oxygen and carbon monoxide on the surface of platinum results in the dissociation of the oxygen molecule into two oxygen atoms (the X* symbol denotes that it is surface-adsorbing) and the formation of CO (Billeter et al., 2000).

$$O_2 + 2^* \rightleftharpoons 2O^*$$
$$CO + {}^* \rightleftharpoons CO^*$$
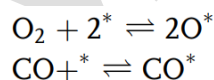
In turn, the adsorbed oxygen atom and carbon monoxide molecule combine on the surface to form CO_2. Because of its great stability and low reactivity, CO_2 interacts poorly with platinum's surface and desorbs very immediately.

$$CO^* + O^* \rightleftharpoons CO_2 + 2^*$$
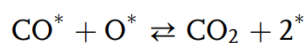
Particularly noteworthy is that the later phase liberates the adsorption sites on the catalyst, so making them available for use in following reaction cycles. On the right-hand side of Figure 1.5, you can see the chemical cycle and a potential energy graph (Vries et al., 1999).

In which part of the loop does the catalyst have the most influence? Assume that the reaction happens in a gaseous state without the aid of a catalyst to accelerate the process. As long as the temperature is elevated enough to produce dissociation of the O_2 molecule into two oxygen atoms, the process will continue (radicals). In the presence of radicals, the reaction between CO and CO_2 takes place very fast.

The activation energy for the gas phase processes will be about equal to the energy necessary to break the very strong O–O bond in oxygen, which is around 500 kJ mol^{-1} at room temperature (Metz et al., 2014).
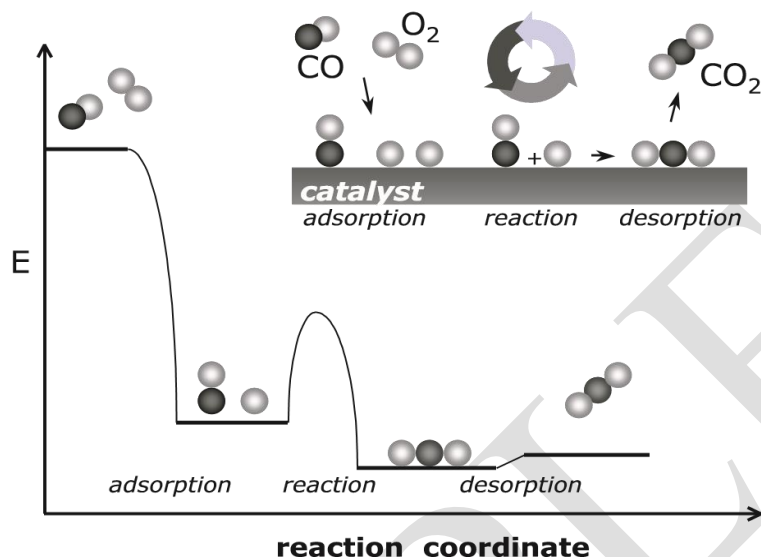

Figure 1.5. *Diagram illustrates the catalytic oxidation of CO by oxygen, showing the reaction cycle and potential energy.*

Source: https://slideplayer.com/slide/10751001/.

However, in a catalytic process, the O_2 molecule dissociates rapidly on the catalyst surface—in fact, it does so without the need for any activation energy. The activation energy is in the range of 50–100 kJ mol^{-1} and is connected to the reaction between adsorbed Carbon monoxide and oxygen atoms in the atmosphere. The desorption of the product molecule CO_2 has a cost of around 16–32 kJ/mol, reliant on the temperature. By comparison the catalyzed reactions with the uncatalyzed reactions, we can see that the catalyst is very efficient at performing the most crucial stage of the gas phase homogeneous process, namely the dissociation of the O–O bond. Therefore, the efficiency with which the Carbon dioxide molecule grows controls the rate at which the full interaction between CO and O_2 occurs. For catalyzed reactions, this is a very common occurrence, which is why the phrase "a catalyst breaks bonds and allows for the production of new ones" is used to describe what is taking place. Because the catalyst's beneficial function is in dissociating a strong link, it is possible that the subsequent processes will go more swiftly even if the catalyst is not present (Sherwood et al., 1997).

1.4. Why Is Catalysis Important?

Because of non-stoichiometric reactions in the laboratory, the industrial sector of the 20th century could never have evolved to its present degree of growth on its own. Several factors in chemical reactions may be controlled to a certain degree, including temperature, concentration, pressure, and time of contact with the reactant. It is necessary to elevate the temperature and pressure in order for

stoichiometric reactions to occur at a pace that is sustainable for the manufacturing process (Field et al., 1990). Constructing reactors where such circumstances can be effectively maintained, on the other hand, is becoming more and more expensive and difficult to do as time goes on. It is also bound by thermodynamic constraints, which preclude the manufacture of certain products at temperatures higher than 600°C due to thermodynamic restraints. For example, at temperatures more than 600°C, the transformation of H_2 and H_2 into ammonia is very hard to do. It is true that greater temperatures are required to break the extraordinarily strong N-N bond in nitrogen dioxide, but that this is not always the case. The absence of catalysts would make many reactions that are frequent in the chemical industry impossible to complete, and several processes would be unproductive if they were not carried out with the help of catalysts (Quesne et al., 2014).

In addition to allowing operations to be carried out in the most favorable thermodynamic domain possible, catalysts also allow them to be carried out at far lower pressures and temperatures than would otherwise be possible in the absence of catalysts. In order for chemical processes to be more cost-effective in respect of both original investment and ongoing operating expenditures, it is necessary to use effective catalysts in conjunction with optimal reactor design and overall plant structure. This, however, is not the case at all (Cornils and Herrmann, 2003).

1.4.1. Catalysis and Green Chemistry

If a technology properly utilizes raw materials while avoiding the use of dangerous and hazardous chemicals and solvents, it is referred to be "green," and waste and undesirable byproducts are kept to a minimum. These criteria are commonly satisfied by catalytic techniques, which are described below. Ethylene glycol (antifreeze), as well as other polyethers and polyurethanes, is produced by the process of selective hydrogenation of ethylene-to-ethylene epoxide. This is an outstanding example of selective ethylene oxidation (SEO) (Figure 1.6).
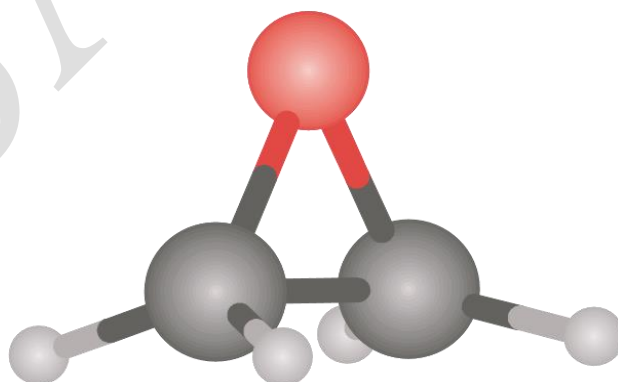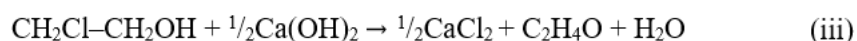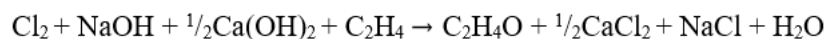

Figure 1.6. *Structure of the chemical industry's most significant intermediate: ethylene epoxide. Source: https://slidetodoc.com/kinetics-rates-and-mechanisms-of-chemical-reactions-kinetics/.*

The epichlorohydrin procedure (the traditional, non-catalytic technique) is a three-step synthesis:

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

$$C_2H_4 + {}^{HOCl} \rightarrow CH_2Cl–CH_2OH \tag{ii}$$

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

or in total:

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

As a consequence, 1 molecule of salt is produced for every molecule of ethylene oxide produced, resulting in a waste issue that was formerly dealt with by disposing of the trash in a river. Of course, such conduct is today considered to be quite unacceptable.

In contrast, while the catalytic technique is easy and environmentally friendly, it does produce a little amount of CO_2. C_2H_4 and O_2 are used to form ethylene oxide, which is produced with a selectivity of around 90%, with only about 10% of the ethylene being converted to CO_2. Silver is used as a catalyst, and it is given a boost by trace amounts of chlorine. The use of catalysts in ethylene oxide production facilities is now mandatory in all of them (Cole-Hamilton, 2003).

1.4.2. E Factors, Atom Efficiency, and Ecological Affability

In a number of organic syntheses, stoichiometric oxidations of organic compounds using potassium permanganate and sodium dichromate, as well as hydrogenations with borohydrides, alkali metals, or zinc, are used. Some chemical reactions, such as acylations with $AlCl_3$ or aromatic nitrations with HNO_3 and H_2SO_4, result in significant amounts of inorganic salts being produced as byproducts.
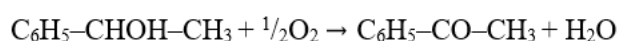
Homogeneous catalysis is mostly (but not exclusively!) limited to fine chemicals, with solvents constituting an extra environmental hazard due to their toxicity. The ideal solvent, according to Sheldon, is none at all, but if one is essential, water is a reasonable alternative (Wang et al., 2012).

Sheldon has developed a variety of metrics for evaluating the efficiency of a response as well as its impact on the environment. When it comes to atom efficiency, it is defined as the ratio of the molecular weight of the goal product to the aggregate molecular weight of all output products. For instance, secondary alcohol's conventional oxidation:

$$3C_6H_5–CHOH–CH_3 + 2CrO_3 + 3H_2SO_4 \rightarrow 3C_6H_5–CO–CH_3 + Cr_2(SO_4)_3 + 6H_2O$$
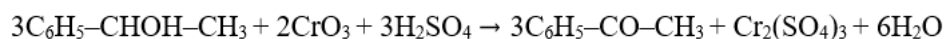
has an atomic efficiency of 360/860 = 42%. Comparatively, the catalytic route:

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

provides an atomic efficiency of 120/138 = 87.0%, with H_2O as the only byproduct. The reverse step (i.e., catalytic hydrogenation) continues with 100% atomic efficiency:

$$C_6H_5–CO–CH_3 + H_2 \rightarrow C_6H_5–CHOH–CH_3$$
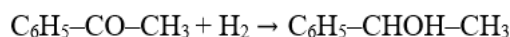
Similarly catalytic carbonylation also shows 100% efficiency:

$$C_6H_5–CHOH–CH_3 + CO \rightarrow C_6H_5–CH(CH_3)COOH$$
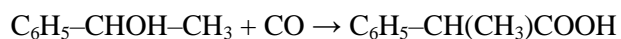
The E factor, which is known as the ratio of the weight of waste to the weight of the intended product, is another important indicator of environmental acceptability in manufacturing. As seen in Table 1.1, pharmaceutical industries produce the greatest amount of waste per unit weight of product produced. 1. Although tom efficiencies and E factors may be calculated from one another, E factors can be much bigger in practice due to lower-than-optimal yields and excessive reagent use. Losses of solvents, as well as energy consumption and CO_2 emissions, should all be taken into consideration (Villa et al., 2000).

Table 1.1. The Environmental Friendliness of Several Chemical Industry Products

Industry Segment	*E* Factor (kg of Waste/kg of Product)	Product Tonnage
Bulk chemicals	<1–5	$10^4–10^6$
Oil refining	<0.1	$10^6–10^8$
Pharmaceuticals	25–>100	$10–10^3$
Fine chemicals	5–50	$10^2–10^4$

It is important to note that Sheldon invented the environmental quotient EQ, which is equal to the E factor times the unfriendliness quotient Q, to explain that it is not just about the amount of trash generated, but also its environmental effect. Pure water has a Q value of 0, whereas hazardous substances have a Q value of 100–1,000. Catalytic routes should be constructed to decrease waste generation. So, for example, the unfriendliness quotient is economically valuable, so creating catalytic alternatives is motivated. Garbage cleanup is time consuming and expensive (George, 1995).

1.4.3. The Chemical Industry

By accelerating reactions, catalysts support industrially significant activities to be performed proficiently and in conditions that are actually achievable. Catalytic routes are often designed in such a manner that efficient use of raw maw materials and waste minimization is achieved. The chemical industry as a consequence has become more dependent on catalysis: catalytic processes are used to make around 85–90% of all commodities, and the proportion is increasing all the time (Ide et al., 2014).

Tables 1.2 and 1.3 highlight the most major industrial processes and chemicals; Table 1.4 and Figure 1.7 outline the top 50 businesses and nations in the chemical sector, respectively; and Table 1.5 summarizes the most significant industrial processes and chemicals.

Table 1.2. Major Processes Involving Heterogeneous Catalysis

Reaction	Catalyst
Crude oil's catalytic cracking	Zeolites

Alkylation	HF, H_2SO_4, solid acids
Naphtha reforming (to gasoline)	Pt, Pt–Ir, Pt–Re
Polymerization of propylene, ethylene, etc.	Cr, $TiCl_x/MgCl_2$
Crude oil's hydrotreating	Ni–Mo, Co–Mo, Ni–W (sulfidic form)
Vinyl chloride (ethylene + Cl_2)	Cu (as chloride)
Epoxidation of ethylene-to-ethylene oxide	Ag
Shift reaction of water-gas	Fe (oxide), Cu–ZnO
Methane steam reforming of to CO + H_2	Ni
Methanation	Ni
Oxidation of ammonia to NO and HNO_3	Pt–Rh
Hydrogenation of vegetable oils	Ni
Synthesis of ammonia	Fe
Oxidation of hydrocarbons and CO (car exhaust)	Pt, Pd
Acrylonitrile synthesis from ammonia and propylene	Bi–Mo, Fe–Sb (oxides)
NOx reduction (in exhaust)	Rh, vanadium oxide
Sulfuric acid	V (oxide)

Every student who wishes to pursue a profession in the chemical design or in chemical engineering should, without a doubt, have a fundamental grasp of catalysis. This is why the authors include catalysis into their respective universities' chemistry courses as early as possible (Table 1.6) (Xiao et al., 1992).

Table 1.3. Organic Chemical Synthesis in the USA and Annual Change in Production Over Years 1995–2005

Organic Chemicals	Change Percentage (%)	Ktons
Propylene	2.8	15,333
Ethylene	1.2	23,974
Ethylene dichloride	3.7	11,308
Ethylbenzene	−1.6	5,251
Urea	−2.4	5,801
Cumene	3.2	3,509
Styrene	−0.2	5,042
1,3-Butadiene	2.1	2,046
Ethylene oxide	−0.9	3,166
Acrylonitrile	−0.9	1,323
Vinyl acetate	0.1	1,327

Benzene (1,000 liters)	−0.8	7,574
Aniline	4.3	964

Table 1.4. Inorganic Chemical Synthesis in the USA and Annual Change in Production Over Years 1995–2005

Inorganic Chemicals	% Change	Ktons
Chlorine	−1.0	10,175
Phosphoric acid	−0.3	11,599
Ammonia	−4.7	9,775
Sodium hydroxide	−2.1	8,384
Sulfuric acid	−1.6	36,520
Nitric acid	−2.3	6,328
Ammonium nitrate	−1.9	6,353
Ammonium sulfate	0.7	2,578
Hydrochloric acid	2.2	4,406

Table 1.5. Organic Chemical (Plastics and Polymers) Synthesis in the USA and Annual Change in Production Over Years 1995–2005

Polymers, Plastics	% Change	Ktons
Polyethylene, linear low density	8.5	5,395
Polyethylene, low density	0.3	3,558
Polyethylene, high density	3.7	7,328
Polystyrene	1.1	2,855
Polypropylene	5.1	8,149
Polyamine, nylons	2.1	568
Polyvinyl chloride and copolymers	2.2	6,921
Styrene polymers (ABS, etc.)	0.3	1,413

Table 1.6. Top Chemical Manufacturers in the World

SL. No.	Company	Country	Chemicals (%)	Chemicals (million $)	Total Sales (million $)
1.	China Petroleum and Chemical	China	21	21,121	100,576
2.	BASF	Germany	82	43,682	53,271
3.	Total	France	16	27,794	173,713

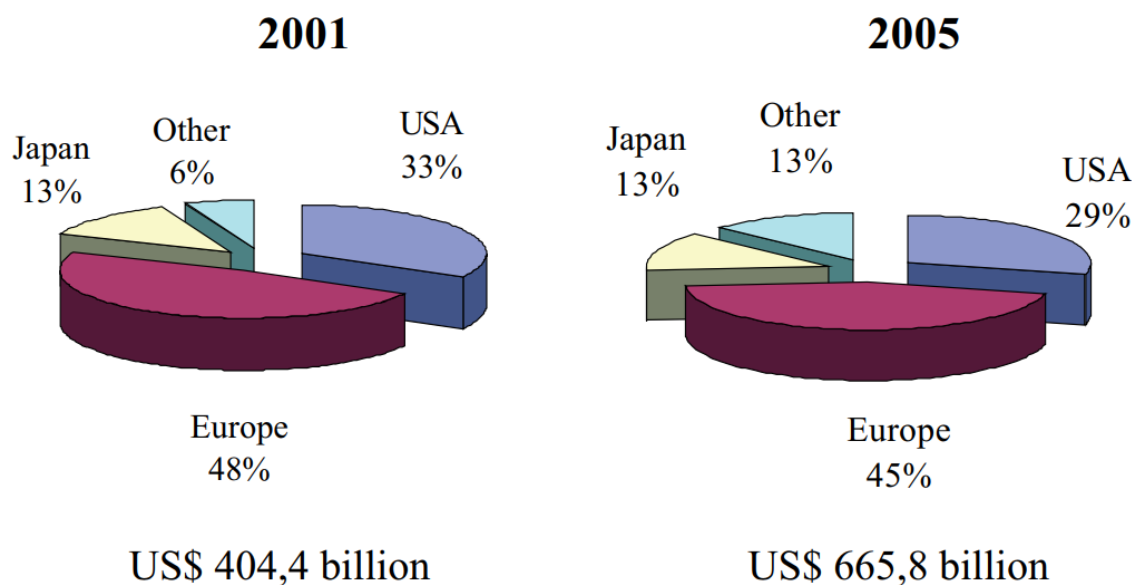|					
4.	Bayer	Germany	61	20,654	33,859
5.	Exxon Mobil	USA	12	31,186	259,883
6.	Royal Dutch Shell	UK/Netherlands	11	34,996	318,145
7.	DuPont	USA	90	25,330	28,144
8.	SABIC	Saudi Arabia	91	18,947	20,821
9.	Dow Chemical	USA	100	46,307	46,307
10.	INEOS Group	UK	100	12,400	12,400
11.	BP	UK	8	20,627	257,838
12.	Lyondell Chemical	USA	100	18,606	18,606
13.	Formosa Plastics	Taiwan	59	18,747	31,775
14.	Degussa	Germany	100	14,630	14,630
15.	Mitsubishi Chemical	Japan	82	17,945	21,884
16.	Huntsman Corp.	USA	100	12,962	12,962
17.	Mitsui Chemicals	Japan	100	13,372	13,372

Figure 1.7. *Europe is the biggest manufacturer of bulk chemicals.*

Source: https://slidetodoc.com/kinetics-rates-and-mechanisms-of-chemical-reactions-kinetics/.