

## Chapter 2. Introduction to Catalysis

### 2.1 Background

The science and technology of catalysis is of great significance as it affects our daily life. Four major sectors of the world economy; petroleum and energy production, chemicals and polymer production, pharmaceutical and food industry and pollution control, involve catalytic processes.

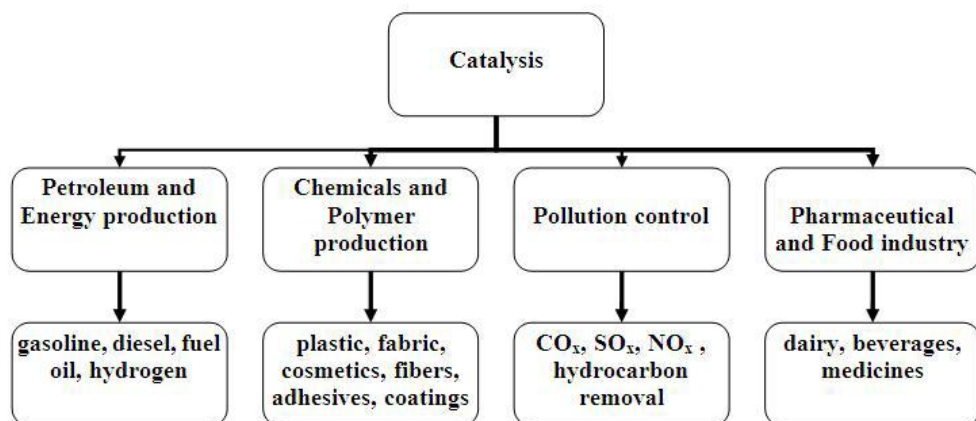


Fig. 1. Four major sectors of world economy that involve catalytic processes

### Catalysts Uses

More than 90 % of industrial processes actually use catalysts in one form or the other. Owing to expanding need of mankind, production in all sectors is increasing at a fast rate and catalysis science has a major contribution in this need.

1. production of fuels such as gasoline, diesel, heating oil, fuel oil, etc.
2. Production of plastics, synthetic rubbers, fabrics, cosmetics, etc.
3. The production of clean energy from renewable energy sources, such as H<sub>2</sub> for fuel cells and transportation fuels from non-edible biomass.
4. Reduction emissions of CO<sub>x</sub>, NO<sub>x</sub> and hydrocarbons from mobile vehicles.
5. Production of the polymers including adhesives, coatings, foams, textile and industrial fibers.
6. The pharmaceutical industry uses catalysts for production of drugs that are used to save lives and improve the health of people.
7. Catalysts are also widely used in food processing.

Increasing catalyst life is another area of importance to maximize catalyst efficiency.

## 2.2 Catalytic reactions

In a thermodynamically feasible chemical reaction, when addition of a small amount of a chemical substance increases the rate of attainment of chemical equilibrium but the substance itself does not undergo any chemical change, then the reaction is called a **catalytic reaction**. The substance that enhances the reaction rate is called a **catalyst**. Catalysts work by providing an alternative mechanism involving a different transition state of lower energy. Thereby, the activation energy of the catalytic reaction is **lowered** compared to the uncatalyzed reaction as shown in Fig 2.

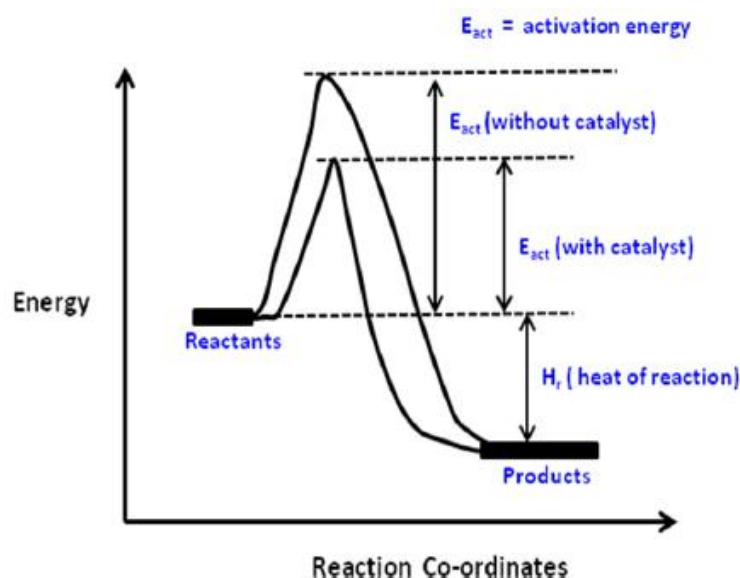
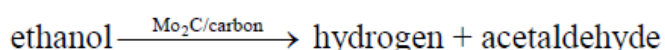
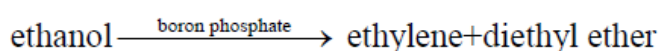


Fig. 2 . Comparison of activation energies of exothermic catalytic and non-catalytic reactions

A catalyst accelerates both the rates of the forward and reverse reaction. Equilibrium of a reversible reaction is not altered by the presence of the catalyst. For example, when oxidation of  $\text{SO}_2$  is carried out in the presence of three different catalysts, namely Pt,  $\text{Fe}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ , the **equilibrium composition** is the same in all three cases. Another important characteristic of catalyst is its effect on **selectivity**. The presence of different catalysts can result in different product distribution from the same starting material. For example, decomposition of ethanol in the presence of different catalysts ( $\text{BPO}_4$  or hemicarbide of molybdenum) results in different products as shown below,



### 2.3 The Concept of 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.

Consider the catalytic reaction between two molecules A and B to give a product P (Fig. 3). 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.

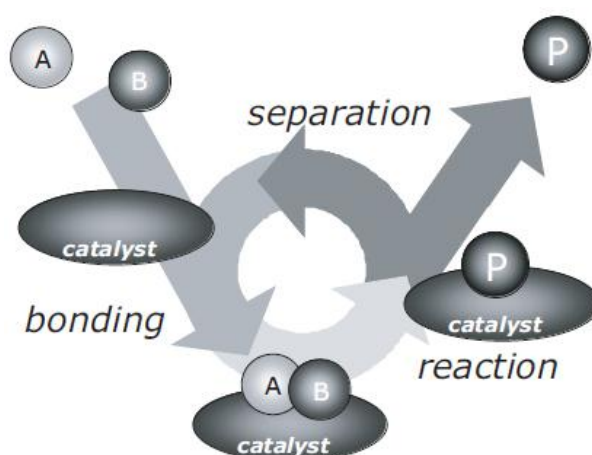


Figure 3. Catalytic reaction sequence of elementary steps.

There are also cases in which the combination of catalyst with reactants or products will not be successful:

1. If the bonding between reactants and catalyst is too weak, there will be hardly any conversion of A and B into product P.
2. 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.
3. 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 the activation energy to form P on the catalyst becomes too high. The catalyst is said to be poisoned by (one) of the reactants.
4. 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.

## 2.4 Types of catalytic reactions

**Homogeneous catalysis:** Reagents and catalyst are all in the same phase (typically all are in solution).

**Heterogeneous catalysis:** Reagents are in a different phase from the catalyst, usually the reagents are gases (or liquids) and the catalyst is solid.

General features:

Heterogeneous	Homogeneous
<ul style="list-style-type: none"><li>Readily separated ✓</li><li>Readily recycled / regenerated ✓</li><li>Long-lived ✓</li><li>Cheap ✓</li></ul>	<ul style="list-style-type: none"><li>Difficult to separate ✗</li><li>Difficult to recover ✗</li><li>Short service life ✗</li><li>Expensive ✗</li></ul>
<ul style="list-style-type: none"><li>Lower rates (diffusion limited) ✗</li><li>Sensitive to poisons ✗</li><li>Lower selectivity ✗</li><li>High energy process ✗</li><li>Poor mechanistic understanding ✗</li></ul>	<ul style="list-style-type: none"><li>Very high rates ✓</li><li>Robust to poisons ✓</li><li>Highly selective ✓</li><li>Mild conditions ✓</li><li>Mechanisms often known ✓</li></ul>

Heterogeneous catalysts are used in refining / bulk chemical syntheses much more than in fine chemicals and pharmaceuticals (which tend to use homogeneous catalysis).

**Biocatalysis:** Using enzymes to catalyze a reaction. Enzymes are natural catalysts, and can be considered as a large protein with structure of very shape-specific active site (i.e. enzymes often match the shape of the substrates they bind to, or the transition state of the reaction they catalyze) as indicated in Fig.4.

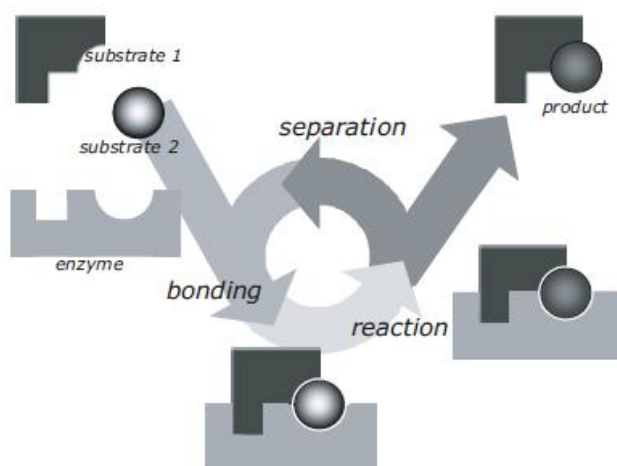
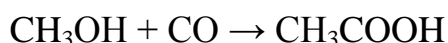


Figure 4. Schematic representation of an enzyme-catalyzed reaction.

### 2.4.1 Homogeneous catalysis

In homogeneous catalysis, both the catalyst and the reactants are in the same phase, i.e. all molecules are in the gas phase, or, more commonly, in the liquid phase, where most industrial homogeneous catalytic processes are carried out in liquid phase. Industrial uses a multitude of homogenous catalysts in all kinds of reactions to produce chemicals. Examples of industrial homogeneous catalytic processes: Ester hydrolysis involving general acid-base catalysts, polyethylene production with organometallic catalysts and enzyme catalyzed processes.

Well-known example is the catalytic carbonylation of methanol to acetic acid:



Using rhodium(I) complex catalyst  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  in solution.

#### Relative significance

Catalytic processes have great significance and about 90 % of all chemical industry involves catalytic processes. Of all the industrial catalytic processes, approximately 80 % involve the use of solid catalysts, 17 % homogeneous catalysts and rest 3 % biocatalysts. Thus, heterogeneous catalysts, particularly solid catalysts, dominate the industrial catalytic processes.

### 2.4.2 Heterogeneous Catalytic Theory

In a heterogeneous catalytic reaction only certain sites on the catalyst surface actually participate in the reaction and these sites are called active sites on the catalysts. These sites may be the unsaturated atoms resulting from surface irregularity or atoms with chemical properties that enable the interaction with the adsorbed reactant atoms or molecules.

Activity of the catalyst is directly proportional to the number of these active sites available on the surface and is often expressed in terms of turnover frequency. Turnover frequency TOF is defined as the number of molecules reacting per active site per second at the condition of experiments. In general, the entire surface of the solid catalyst is not responsible for catalyzing any reaction, but only the certain sites.

A solid catalytic reaction  $A \rightarrow B$  goes through the following steps (also the steps are illustrated in Fig. 5):

1. Transportation of reactant (A) from bulk fluid to pore entry on the external surface of catalysts pellets.
2. Diffusion of the reactant (A) from the pore entry through the catalyst pores to the immediate vicinity of internal catalytic surface.
3. Adsorption of reactant (A) onto the catalyst surface.
4. Reaction of (A) on the catalyst surface producing product (B).
5. Desorption of the product (B) from the surface.
6. Diffusion of the product (B) from interior part of the pores to the pore entry on the external surface
7. Transfer of the product (B) from pore entry on the external surface to the bulk fluid.

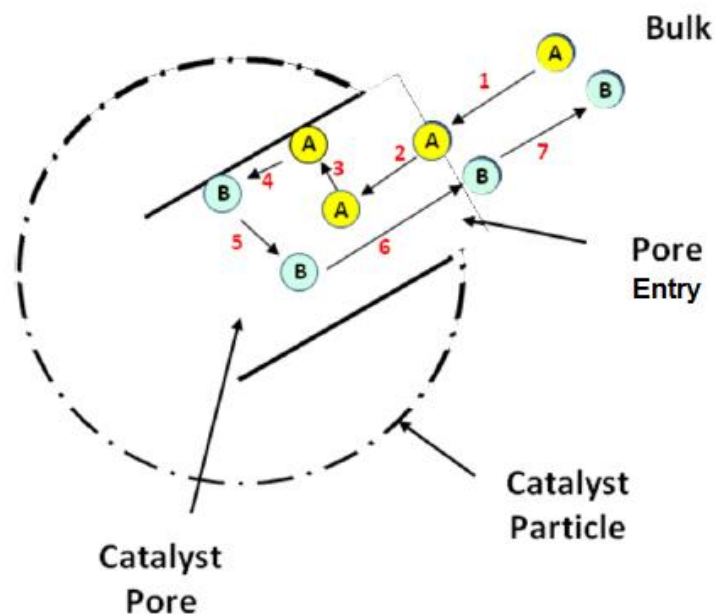


Fig. 5. Steps in solid catalytic reactions.

The overall rate of reaction is mostly influenced with the rate of steps in the mechanism:

1. When the mass transfer and diffusion steps [1,2,6,7] are very fast compared to adsorption and reaction steps [3,4,5], concentration in the immediate vicinity of the active sites is the same that in the bulk fluid. Consequently, the transport or diffusion steps do not affect the overall rate of the reaction.

2. Alternatively, if diffusion steps [2,6] and reaction [4] are fast compared to the mass transfer steps [1,7], then mass transfer does affect the rate of reaction.

3. When mass transfer from the bulk phase to the pore entry [1] is slow and affects the reaction rate, then changing the flow conditions past the catalyst should change the overall reaction rate.

4. In case of porous catalysts, diffusion within the catalyst pores [2,6] may limit the reaction rate. Under this condition external flow does not affect the reaction rate but internal diffusion does affect.

### Why adsorption takes place on solid surface?

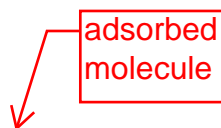
In the bulk of the adsorbent, the molecules are associated with their adjacent equally in all direction and the molecular forces are therefore balanced. However on the adsorbent surface, the molecules are bounded to the inner molecules at one side leaving unbalanced molecular forces on the other side. These unbalanced molecular forces on adsorbent surfaces (catalyst) create the attractive force for the adsorbate molecules approaching the surface. These molecular forces are weak in nature and called van der Waals attraction forces.

## 2.5 Types of adsorption

Depending on the nature of interaction, the adsorption can be of two types:

1. *Physisorption*

2. *Chemisorption*



The phenomenon of adsorbate molecules attaching themselves to adsorbent surface under the influence of van der Waals forces is called physisorption or physical adsorption. The van der Waals forces mainly consist of dipole-dipole interactions.

This is an exothermic process with a low enthalpy change known as heat of adsorption.

Chemisorption (or chemical adsorption) involves the formation of strong bonds between adsorbate molecules and specific surface locations known as active sites.

result when two dipolar molecules interact with each other through space. When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule



## Chemisorption Characteristics

1. Chemisorption process is selective and an adsorbate molecule will chemisorbed only on selected adsorbent. Hence all adsorbate will not be chemisorbed on all adsorbent surfaces.
2. The strong interaction between the adsorbate molecules and the adsorbent surface creates new types of electronic bonds and the process is irreversible.
3. The energy of chemisorption is of the same order of magnitude as the enthalpy change in a chemical reaction between a solid and a fluid: thus chemisorption, like chemical reactions in general, may be exothermic or endothermic and the magnitudes of the enthalpy changes may range from very small to very large.
4. The elementary step in chemisorption often involves an activation energy, where the activation energy for adsorption is large (activated adsorption).

The adsorption processes types are shown in Fig 6. with following:

The Fig. 6(a) depicts the situation when the adsorbate molecule approach any adsorbent surface under the influence of attractive forces created by the unbalanced molecular forces on adsorbent surfaces.

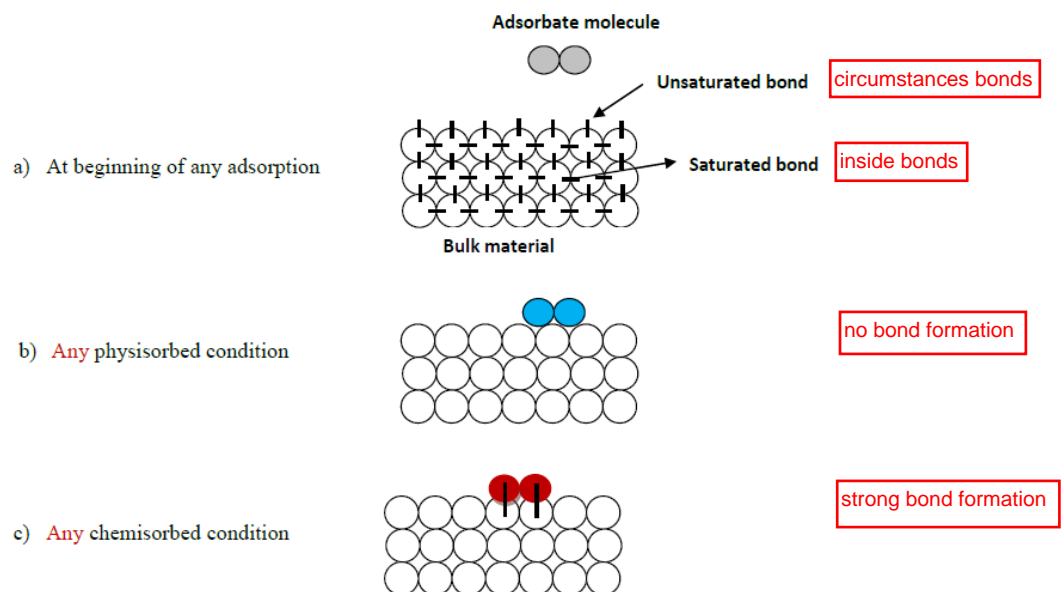


Fig. 6. Schematic representation of different adsorption processes

The Fig. 6(b) represents the phenomenon, when any molecule is physisorbed on surface by van der Waals forces. No bond formation occurs in this situation.



A chemisorption situation is represented in Fig. 6(c) when there is a chemical bond formation between adsorbate and adsorbent molecules. As discussed above, the adsorbate molecule will be chemisorbed only on selected adsorbent surface with which it can interact significantly.

### Examples :

Physisorption : Adsorption of nitrogen on carbon or alumina.

Chemisorption : Adsorption of hydrogen on active platinum sites of any support.

### Physisorption versus Chemisorption

1. Since physisorption involves only weak molecular interaction, the associated enthalpy changes are small (in the range of 10 to 40 kJ /mol) . On the other hand, for chemisorption the enthalpy change is quite large and can range from 80-400 kJ /mol.
2. In physisorption, the molecules are adsorbed on surface by weak interaction. With increase in temperature, adsorbed molecules gain excess energy and their tendency to escape from the surface increases. Hence volume of gas adsorbed on the surface decreases with temperature as shown in Fig. 7. The chemisorption involves higher interaction energy between adsorbate and adsorbent molecules and hence is favored by temperature rise.

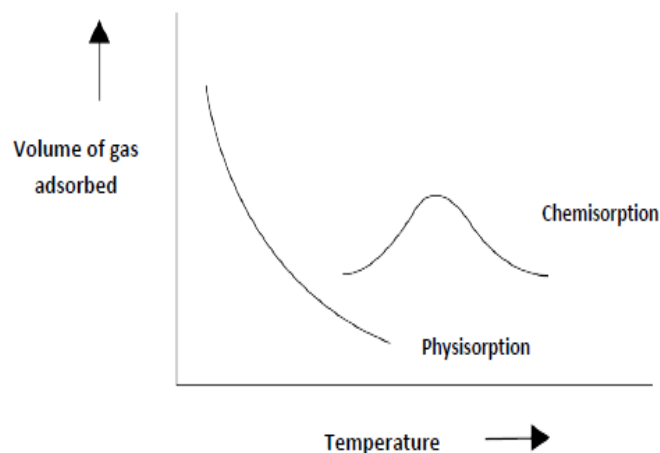


Fig. 7. Volume of gas adsorbed vs. temperature for physisorption and chemisorption processes

3. In case of chemisorption, since there is electronic interaction between adsorbate and adsorbent molecules, only a monolayer of adsorbate can be formed on the adsorbent surface. In case of physisorption, the first monolayer formed on the surface

of the adsorbent can act as adsorbing surface for formation of next layer of adsorbate and so on. This phenomenon is called multilayer adsorption. The formation of monolayer and multilayers of the adsorbed molecules on a surface is shown in Fig. 8.

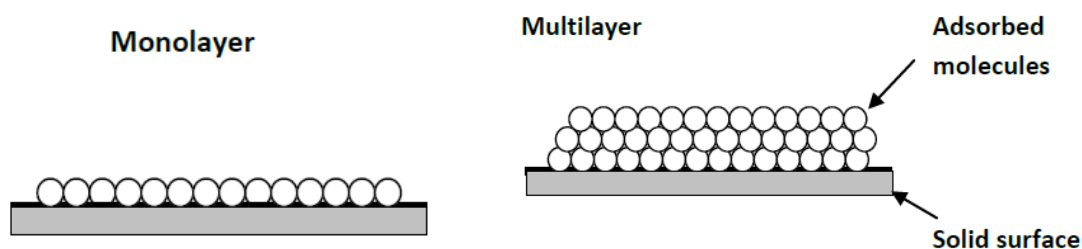


Fig. 8 . Monolayer and multilayer formation of the adsorbed molecules on a surface

**4.** Chemisorption is specific for adsorbate and adsorbent pair. Specific solid adsorbent can undergo electronic interaction only with specific adsorbate gas molecule.

**5.** Physisorption is highly reversible while chemisorption can be irreversible.

**6.** Physisorption is important for estimating the total surface area. It also provides a basis for estimating the pore volume and pore size distributions. On the other hand, chemisorption is important in estimation of area of catalytic active sites as well as its dispersion.

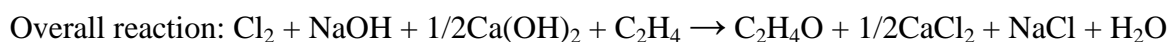
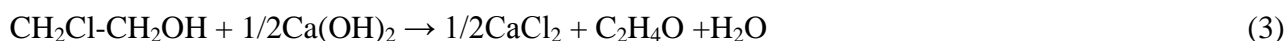
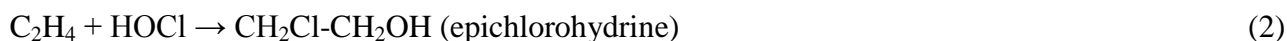
## 2.6 Catalysis and Green Chemistry

Environmental technology, green technology or clean technology is a general term used to describe products, processes or services that reduce waste and require as few non-renewable resources as possible. This technology is considered environmentally friendly based on its production process or supply chain; such that the use of toxic and hazardous reagents and solvents can be avoided while formation of waste or undesirable byproducts is minimized.

### Industrial Example 1

The selective oxidation of ethylene to ethylene epoxide, is an important intermediate towards ethylene glycol (antifreeze) and various polyethers and polyurethanes:

### 1. Epichlorohydrine process (non-catalytic route)



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.

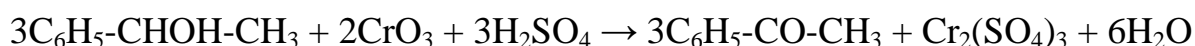
### 2. The catalytic route

This route is simple and clean, although it does produce a small amount of CO<sub>2</sub>. Using silver, promoted by small amounts of chlorine, as the catalyst, ethylene oxide is formed directly from C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub> at a selectivity of around 90 %, with about 10% of the ethylene ending up as CO<sub>2</sub>. Nowadays all production facilities for ethylene oxide use catalysts.

There are several indicators to measure the efficiency and environmental impact of a reaction:

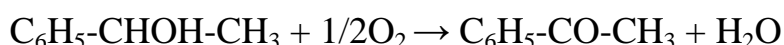
**2.6.1 Atom Efficiency:** It is the molecular weight of the desired product divided by the total molecular weight of all products. So, atom efficiency is a measure of the completion of a reaction and it is, in contrast to percent yield, takes into account all of the atoms involved in the reaction.

**Example 2:** the conventional oxidation of a secondary alcohol to acetophenone



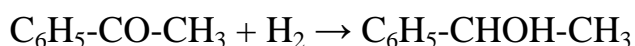
has an atom efficiency of  $360/(3 \times 120 + 392 + 6 \times 18) = 360/860 = 42\%$ .

By contrast, the catalytic route:

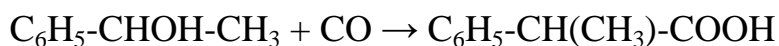


offers an atom efficiency of  $120/(120 + 18) = 120/138 = 87\%$ , with water as the only byproduct.

**Example 3:** The reverse step, a catalytic hydrogenation of acetophenone, proceeds with 100% atom efficiency:



as does the catalytic carbonylation of this molecule to give 2-phenylpropanoic acid:



Another useful indicator of environmental acceptability is the E-Factor.

**2.6.2 E-Factor:** It is defined as the weight of waste or undesirable byproduct divided by the weight of the desired product. Tab. 1 shows, the production of fine chemicals and pharmaceuticals generate the highest amounts of waste per unit weight of product.

Table 1. Environmental acceptability of products in different segments of the chemical industry

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

For generating 1 kilogram of waste for every 5 kilograms of final product, the E-Factor is 1/5 or 0.2. The lower E-Factor, the better performing product.

**Example 4:**

e.g. esterification of n-butanol with acetic acid



Typical procedure: 37g butanol, 60 g glacial acetic acid and 3 drops of  $\text{H}_2\text{SO}_4$  are mixed together. The reaction mixture is then poured into 250  $\text{cm}^3$  water. The organic layer is separated and washed again with water (100  $\text{cm}^3$ ), saturated  $\text{NaHCO}_3$  (25  $\text{cm}^3$ ) and more water (25  $\text{cm}^3$ ). The crude ester is then dried over anhydrous  $\text{Na}_2\text{SO}_4$  (5 g), and then distilled. Yield = 40 g (69 %).

Total amount of reactants = 37+60+250+100+25+25+5= 502 gm

Amount of product = 40 gm

Amount of waste = 502-40 = 462 gm

E-Factor = Amount of waste/Amount of product = 462/40 = 11.55

**Example 5:**

The catalytic reaction of Phenyl iodide with copper gives biphenyl and copper iodide:



Here no reactant is left over, since the conversion is 100%.

For every mol of biphenyl product, we obtain one mol of CuI<sub>2</sub> waste. First, calculate the number of moles in one kg of product:

Mwt of biphenyl, or C<sub>12</sub>H<sub>10</sub>, = 154 gm/mol, so 1 kg biphenyl = 6.5 mol biphenyl.

This means that every kg of biphenyl product will give also 6.5 mol of CuI<sub>2</sub> (Mwt = 317.5 gm/mol), which is equivalent to 6.5 × 317.5 = 2063.75 gm CuI<sub>2</sub>.

E-Factor = Amount of waste/Amount of product = 2.06375/1000 = 2.064

### Example 6:

**The catalytic reaction of Phenyl bromide with copper gives biphenyl and copper bromide:**



Here some reactants is left over, since the conversion is 85%.

Importantly, this reaction does not give 100% conversion. Since the E-factor is simply the quotient kg waste/kg product, everything which is not “product” is defined as “waste”.

Thus, for every two moles of C<sub>6</sub>H<sub>5</sub>Br and one mol of Cu, obtain 0.85 moles of biphenyl and 0.85 moles of CuBr<sub>2</sub> with waste of unreacted C<sub>6</sub>H<sub>5</sub>Br and Cu.

The overall reaction equation may be written as:

Reaction:	$2\text{C}_6\text{H}_5\text{Br} + \text{Cu} \rightarrow \text{C}_6\text{H}_5\text{-C}_6\text{H}_5 + \text{CuBr}_2$			
Stoichiometric	2	1	1	1
Reactants and products	2×0.85	1×0.85	1×0.85	1×0.85
Unreacted materials	2×0.15	1×0.15		

So, Biphenyl product = 1×0.85× 154 = 130.9 gm

Waste CuBr<sub>2</sub> = 1×0.85 ×223 = 189.5 gm

Waste Cu = 1×0.15 ×63.5 = 9.5 gm

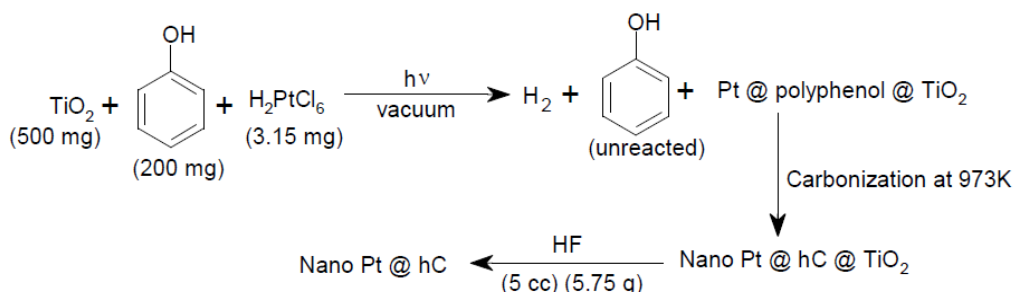
Waste C<sub>6</sub>H<sub>5</sub>Br = 2×0.15× 157 = 47.1 gm

Total amount of waste material = 189.5+9.5+47.1 = 246.1 gm

E-Factor = Amount of waste/Amount of product = 246.1/130.9 = 1.88

### Example 7:

The photocatalytic oxidation of phenol in aqueous suspension of TiO<sub>2</sub> and in the presence of chloroplatinic acid with UV source, according to the following reaction:



Total amount of reactants: 500 mg + 200 mg + 3.15 mg + 5.75 g = 6.48 g

Amount of final product: 203 mg., assuming that the same amount of phenol and platinum salt used in the beginning are retained in the final catalyst.

Amount of waste: (6.48 – 0.203) g = 6.277 g

E-Factor = Amount of waste/Amount of product = 6.277/0.203 = 30.92

## 2.7 The Chemical Industry Catalysis

Catalysts accelerate reactions and thus enable industrially important reactions to be carried out efficiently under practically attainable conditions. Very often, catalytic routes can be designed such that raw materials are used efficiently and waste production is minimized. Consequently, the chemical industry is largely based upon catalysis: Roughly 85–90% of all products are made in catalytic processes (Table-2), and the percentage is increasing steadily.

Table 2. Largest processes based on heterogeneous catalysis.

Reaction	Catalyst
Catalytic cracking of crude oil	Zeolites
Hydrotreating of crude oil	Co–Mo, Ni–Mo, Ni–W (sulfidic form)
Reforming of naphtha (to gasoline)	Pt, Pt–Re, Pt–Ir
Alkylation	H <sub>2</sub> SO <sub>4</sub> , HF, solid acids
Polymerization of ethylene, propylene, a.o.	Cr, TiCl <sub>x</sub> /MgCl <sub>2</sub>
Ethylene epoxidation to ethylene oxide	Ag
Vinyl chloride (ethylene + Cl <sub>2</sub> )	Cu (as chloride)
Steam reforming of methane to CO + H <sub>2</sub>	Ni
Water-gas shift reaction	Fe (oxide), Cu–ZnO
Methanation	Ni
Ammonia synthesis	Fe
Ammonia oxidation to NO and HNO <sub>3</sub>	Pt–Rh
Acrylonitrile from propylene and ammonia	Bi–Mo, Fe–Sb (oxides)
Hydrogenation of vegetable oils	Ni
Sulfuric acid	V (oxide)
Oxidation of CO & hydrocarbons (car exhaust)	Pt, Pd
Reduction of NO <sub>x</sub> (in exhaust)	Rh, vanadium oxide