

**Natubhai V. Patel College of Pure & Applied Sciences**

**S. Y. B.Sc. (Industrial chemistry)**

**C-214: Chemical Process Industries**

**UNIT – 6A**

**Syllabus**

**Catalysis:** Types : Homogeneous and heterogeneous, basic Principles, Mechanism, factors affecting the performance, phase transfer catalysis, enzyme catalysis reactions, industrially important reactions, industrially important catalyst – their classification and preparation

**CATALYSIS AND CATALYST**

**6.0 INTRODUCTION**

**Berzelius J.J.** (1836) realized that, there are substances which, **increases rate** of a reaction **without** themselves being **consumed**. He believed that function of such a substance was to loosen the bonds which hold the atoms in the reacting molecules together. Thus he coined the term Catalysis (Greek-Kata = wholly, Lein = to loosen).

There is no doubt, that usually a catalyst accelerates a reaction as was originally thought by Berzelius. But A number of cases are now known where the catalyst definitely retards (slows down) the rate-of a reaction.

**Catalyst** is defined as a **substance**, which **alters the rate of** a chemical **reaction**, itself remaining **chemically unchanged** at the end of the reaction. The **process** is called **Catalysis**.

As evident from the above definition, a catalyst may increase or decrease the rate of a reaction.

A catalyst which **enhances** the rate of a reaction is called a **Positive Catalyst** and the process Positive Catalysis or simply Catalysis.

A catalyst which **retards** the rate of a reaction is called a **Negative Catalyst** and the process Negative Catalysis.

We will first proceed to discuss 'positive catalysis' or catalysis as it is commonly designated.

**6.1 TYPES OF CATALYSIS**

There are two main types of catalysis

1. Homogeneous catalysis
2. Heterogeneous catalysis

Also, there is a third type of catalysis known as **Enzyme catalysis** which is largely of biological interest. This will be discussed separately at a later stage.

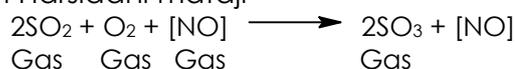
**6.1.1 Homogeneous catalysis**

In homogenous catalysis, the **catalyst** is in the **same phase** as the **reactants** and is evenly distributed throughout. This type of catalysis can occur in gas phase or the liquid (solution) phase.

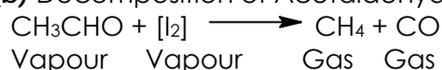
**(1) Examples of homogenous catalysis in gas phase**

**(a)** Oxidation of sulfur dioxide (SO<sub>2</sub>) to sulfur trioxide (SO<sub>3</sub>) with nitric oxide (NO) as catalyst

Jai Shri Harsiddhi mataji



**(b)** Decomposition of Acetaldehyde (CH<sub>3</sub>CHO) with iodine (I<sub>2</sub>) as catalyst



**(2) Examples of homogeneous catalysis in solution phase**

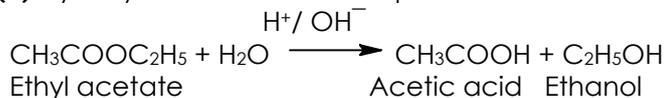
Many reactions in solutions are catalyzed by acids ( $H^+$ ) and bases ( $OH^-$ )

- (a) Hydrolysis of cane-sugar in aqueous solution in presence of mineral acid as catalyst



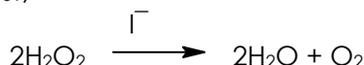
Cane sugar                      [H<sub>2</sub>SO<sub>4</sub>]      Glucose      Fructose

- (b) Hydrolysis of an ester in the presence of acid or alkali,



Ethyl acetate    Acetic acid      Ethanol

- (c) Decomposition of Hydrogen peroxide ( $H_2O_2$ ) in the presence of iodide ion ( $I^-$ ) as catalyst,

**6.1.2 Heterogeneous catalysis**

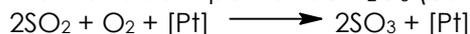
The Catalysis, in which the **catalyst** is in a **different physical phase** from the **reactant**, is termed **Heterogeneous catalysis**. The most important of such reactions are those in which the **reactants** are in the **gas** phase, while the **catalyst** is a **solid**. The process is called **Contact catalysis** since the reaction occurs by contact of reactants with the catalyst surface. In contact catalysis, usually the catalyst is a finely divided metal or gauze. This form of catalysis has great industrial importance.

**Examples of Heterogeneous Catalysis**

Some examples of heterogenous catalysis with reactants in the gas, liquid or the solid phase are listed below.

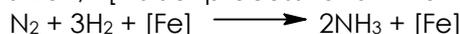
**(1) Heterogeneous catalysis with gaseous reactants (Contact catalysis)**

- (a) Combination of sulfur dioxide ( $SO_2$ ) and oxygen in the presence of finely divided platinum or vanadium pentoxide  $V_2O_5$  (contact process for sulfuric acid)



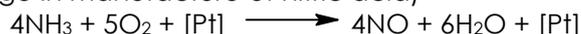
Gas    Gas    Solid

- (b) Combination of Nitrogen and Hydrogen to form ammonia in the presence of finely divided iron, [Haber process for ammonia]



Gas    Gas    Solid

- (c) Oxidation of ammonia to nitric oxide (NO) in the presence of platinum gauze (A stage in manufacture of nitric acid)



Gas    Gas    Solid

- (d) Hydrogenation reactions of unsaturated organic compound are catalyzed by finely divided Nickel,

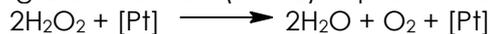


Ethene(g)    Gas    Solid                      Ethane

Vegetable oils are triesters of glycerin with higher unsaturated acid (oleic acid). When hydrogen is passed through the vegetable oil in the presence of nickel, the carbon-carbon double bonds of the acid portions are hydrogenated to yield solid fats (Vanaspati ghee).

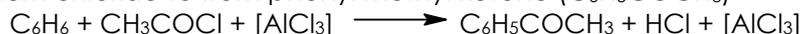
**(2) Heterogeneous catalysis with liquid reactants**

- (a) The decomposition of aqueous solutions of hydrogen peroxide ( $H_2O_2$ ) is catalyzed by manganese dioxide ( $MnO_2$ ) or platinum in colloidal form.



Liquid    Solid

- (b) Benzene and ethenoyl chloride ( $CH_3COCl$ ) react in the presence of anhydrous aluminum chloride to form phenyl methyl ketone ( $C_6H_5COCH_3$ )



Liquid    Liquid                      Solid

**(3) Heterogeneous catalysis with Solid reactant**

The decomposition of potassium chlorate ( $KClO_3$ ) is catalyzed by manganese dioxide ( $MnO_2$ )



## 6.2 CHARACTERISTICS OF CATALYTIC REACTIONS

Although there are different types of catalytic reactions, the following features or characteristic, are common to most of them. These features are often referred to as the **criteria of catalysis**

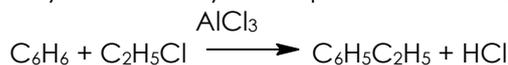
**(1) A catalyst remains unchanged in mass and chemical composition at the end of reaction**

Qualitative and Quantitative analysis shows that catalyst undergoes **no change** in **mass or chemical nature** however; it may undergo a **physical-change**. Thus, granular manganese dioxide ( $\text{MnO}_2$ ) used as catalyst in the thermal decomposition of potassium chlorate is left as a fine powder at the end of the reaction.

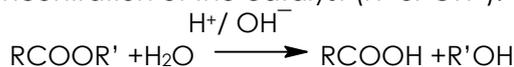
**(2) A small quantity of catalyst is generally needed to produce almost unlimited reaction**

Sometimes a **trace** of a metal catalyst is required to affect **very large, amount** of **reactant**. For example, one ten-millionth of its mass of finely divided platinum is all that is needed to catalyze the decomposition of hydrogen peroxide.

On the other hand, there are catalysts, which need to be present in relatively large amount to be effective. Thus in Fredel craft reaction, anhydrous aluminum chloride functions as a catalyst effectively when present to the extent of 30% of the mass of benzene.



For the acid and alkaline hydrolysis of an ester the rate of reaction is proportional to the concentration of the catalyst ( $\text{H}^+$  or  $\text{OH}^-$ ).

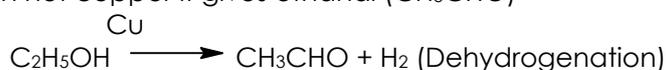
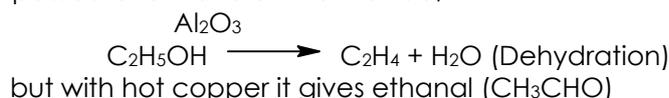


**(3) A catalyst is more effective when finely divided**

In heterogeneous catalysis the solid catalyst is more effective when in a state of **fine subdivision** than it is used in bulk. Thus a lump of platinum will have much less catalytic activity than colloidal or platinised asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel.

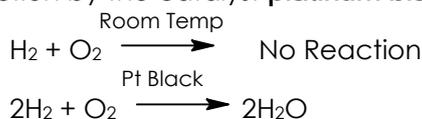
**(4) A catalyst is specific in its action**

While a particular catalyst works for one reaction, it will not necessarily work for another reaction. **Different catalysts**, moreover, can bring about completely **different reactions** for the **same substance**. For example, ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) gives ethane ( $\text{C}_2\text{H}_4$ ) when passed over hot aluminum oxide,



**(5) A catalyst in general, cannot initiate a reaction**

In most cases, a **catalyst speeds up** a reaction already **in progress** and **does not initiate** (or start) the **reaction**. But there are certain reactions where the reactants do not combine for very long period (perhaps years). For example, a mixture of hydrogen and oxygen, which remains unchanged almost indefinitely at room temperature, can be brought to reaction by the catalyst **platinum black**, in a few seconds.



Thus, it is now considered that **the catalyst can initiate reaction**. According to this view, the reacting molecules (in the absence of catalyst) do not possess minimum kinetic energies for successful collisions. The molecules rebound from collisions without reacting at all.

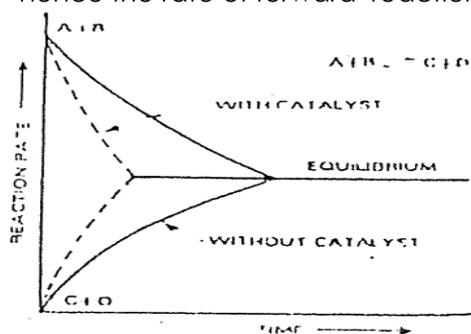
**(6) A catalyst does not affect the final position of equilibrium, although it shortens the time required to establish the equilibrium**

It implies that in a **reversible reaction** the catalyst **accelerate** the forward and reverse reaction **equally**. Thus the ratio of the rates of two opposing reaction i.e. equilibrium constant, remains unchanged

The effect of a catalyst on the time required for equilibrium to be established for the reaction



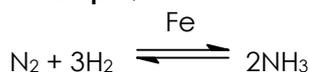
is illustrated in Figure to start with, the concentration of A and B are at the maximum and hence the rate of forward reaction maximum.



**Figure: 1** The effect of catalyst on time required for equilibrium to be established

As the time passes, the rate of the reaction decreases till the equilibrium is established. For the, reverse reaction the initial concentrations of C and D are zero, and the rate of reaction is lowest As the time passes, the rate of reaction increases till the equilibrium is established. Similar curves of the rates of reactions with the catalyst show that the rates of the forward reaction and the reverse reaction are altered equally but the equilibrium is established in a much shorter time.

**For example**, in the Haber process for ammonia,



The reaction is very slow. In the presence of the catalyst, the equilibrium is reached much sooner but the percentage yield remains unchanged. The **iron catalyst shortens the time** to attain **equilibrium** but **cannot alter** the percentage **yield**.

Energy considerations also show that the catalyst cannot change the final state of equilibrium. Suppose the catalyst accelerates the forward reaction more than the reverse reaction. This will shift the equilibrium point, which cannot happen without the supply of energy to the system. But a catalyst unchanged, in mass and composition at the end of the reaction, cannot supply the required energy.

**(7) Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction without a catalyst**

We have already studied the effect of temperature change on reversible reactions under Le Chatelier Principle.

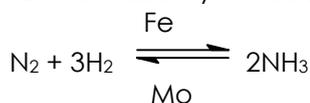
Some **catalysts** are, however, **physically altered** by a **rise in temperature** and hence their catalytic **activity** may be **decreased**. This is particularly true with colloidal solutions like that of platinum, since a rise in the temperature may cause their coagulation. In such a case, the rate of reaction increases up to a certain point and then gradually decreases. The rate of reaction is maximum at a particular temperature; the **Optimum temperature**.

### 6.3 PROMOTERS

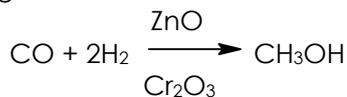
The activity of a catalyst can often be increased by addition of in small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble-catalyst.

**A substance, which though itself not a catalyst, promotes the activity of a catalyst, is called a promoter.**

**Example:** Molybdenum (Mo) or aluminum oxide ( $Al_2O_3$ ) promotes the activity of iron catalyst in the haber synthesis for the manufacture of ammonia.



In some reactions, mixtures of catalyst are used to obtain the maximum catalytic efficiency. For example, in the synthesis of methanol ( $\text{CH}_3\text{OH}$ ) from carbon monoxide and hydrogen, a mixture of zinc and chromium oxide is used as a catalyst.

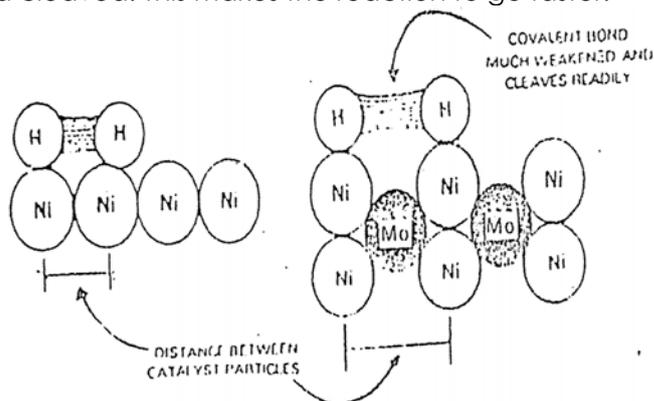


### Explanation

The theory of promotion of a catalyst is not clearly understood. Presumably

#### (1) Change of Lattice spacing

The **lattice spacing** of the **catalyst** is **changed**, thus **enhancing** the **spaces** between the catalyst **particles**. The adsorbed molecules of the reactant (say  $\text{H}_2$ ) are further weakened and cleaved. This makes the reaction to go faster.



**Figure: 2** How the change of crystal lattice spacing of catalyst makes the reaction to go further

#### (2) Increase of Peaks and Cracks

The presence of the promoter increases the peaks and cracks on the catalyst surface. This increases the concentration of the reactant molecules and hence the rate of reaction.

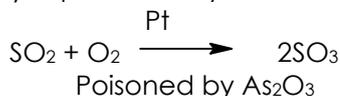
The phenomenon of promotion is a common feature of heterogeneous catalysis.

## 6.4 CATALYTIC POISONING

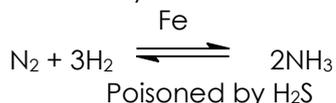
Very often, a heterogeneous catalyst is rendered ineffective by the presence of small amounts of impurities in the reactants.

**A substance, which destroys the activity of the catalyst to accelerate a reaction, is called a poison and the process is called Catalytic poisoning.**

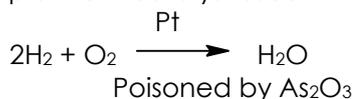
**Examples (1)** The platinum catalyst used in the oxidation of sulfur dioxide (Contact process), is poisoned by arsenic oxide ( $\text{As}_2\text{O}_3$ )



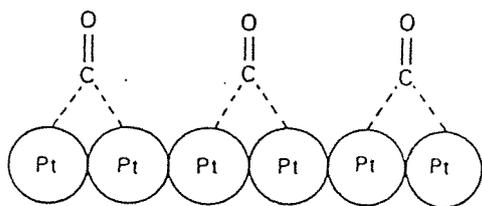
**(2)** The iron catalyst used in the synthesis of ammonia (Haber process) is poisoned by  $\text{H}_2\text{S}$



**(3)** The platinum catalyst used in the oxidation of hydrogen is poisoned by  $\text{As}_2\text{O}_3$  or CO

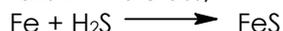


**Explanation:** The poison is adsorbed on the catalyst surface in preference to the reactants. Even a monomolecular layer renders the surface unavailable for further adsorption of the reactants. The poisoning by  $\text{As}_2\text{O}_3$  or CO appears to be of this kind.



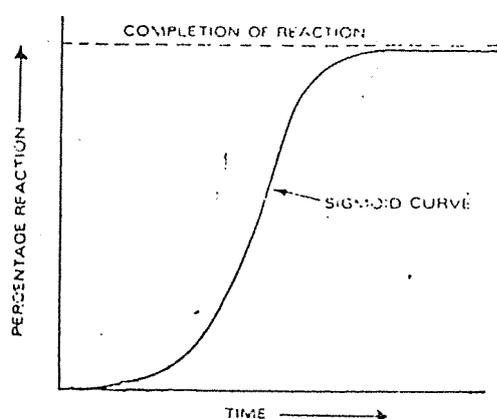
**Figure: 3** Poisoning of platinum catalyst by carbon monoxide

The catalyst may combine chemically with the impurity. The poisoning of iron catalyst by  $\text{H}_2\text{S}$  falls in this class,



### 6.5 AUTO CATALYSIS

When **one of the products** of a reaction itself acts as a **catalyst** for that reaction the phenomenon is called **auto-catalysis**.



**Figure: 4** Curve showing the rise of rate of reaction with time

In auto-catalysis, the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily (See figure:4). The curve plotted between reaction rate and time shows a maximum when the reaction is complete.

**Examples:**

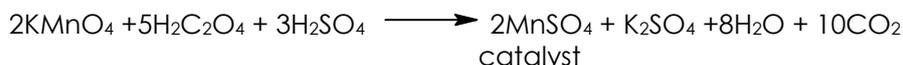
#### (1) Hydrolysis of an ester

The hydrolysis of ethyl acetate forms acetic acid ( $\text{CH}_3\text{COOH}$ ) and ethanol. Of these products acetic acid acts as a catalyst for the reaction.



#### (2) Oxidation of oxalic acid

When oxalic acid is oxidized by acidified potassium permanganate, manganese sulfate produced during the reaction acts as catalyst for the reaction.



#### (3) Decomposition of arsine

The free arsenic produced by the decomposition of arsine ( $\text{AsH}_3$ ) auto-catalyses the reaction.



### 6.6 NEGATIVE CATALYSIS

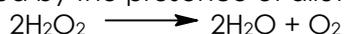
When a catalyst reduces the rate of a reaction, it is called a **Negative catalyst** or **Inhibitor**. This phenomenon is called Negative catalysis or Inhibition. Negative catalysis is useful to slow down or stop altogether an unwanted reaction.

**Example: (1)** Oxidation of trichloromethane ( $\text{CHCl}_3$ ). Trichloromethane (or chloroform) is used as an anesthetic upon oxidation by air, it forms carbonyl chloride ( $\text{COCl}_2$ ) which is a poisonous substance.



2 % of ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) when added to chloroform act as a negative catalyst and suppresses the formation of carbonyl chloride.

**(2)** Decomposition of Hydrogen peroxide. The decomposition of hydrogen peroxide is retarded by the presence of dilute acids or glycerol.



**(3)** Lead tetraethyl as antiknock. When lead tetraethyl  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , is added to petrol, it retards the too rapid or explosive combustion of the fuel which is responsible for knocking of the engine.

**Explanation**

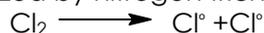
The mechanism of negative catalysis could be different for different reactions

**(1) By poisoning a catalyst**

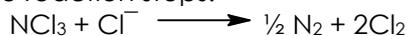
A negative catalyst may function by poisoning a catalyst which already happens to be present in the reaction mixture **for example**, the traces of alkali dissolved from the glass of the container; catalyze the decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). But the addition of an acid would destroy the alkali catalyst and thus prevent decomposition.

**(2) By breaking a chain reaction**

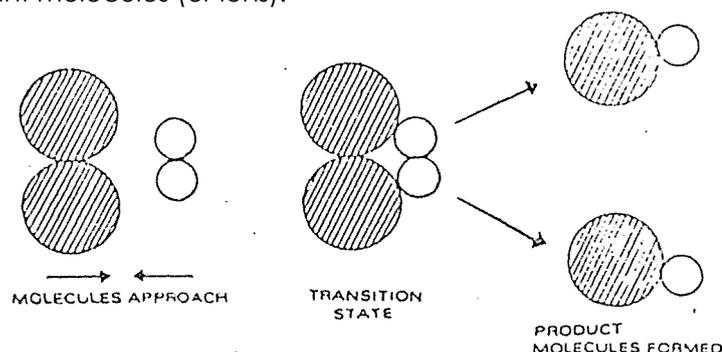
In some cases, negative catalysts are believed to operate by breaking the chain of reactions. **For example**, the combustion of  $\text{H}_2$  and  $\text{Cl}_2$  which is a chain reaction is negatively catalyzed by nitrogen trichloride ( $\text{NCl}_3$ ).



$\text{NCl}_3$  breaks the chain of reactions by absorbing the propagating species ( $\text{Cl}^\bullet$  or  $\text{Cl}^-$ ), and the reaction stops.

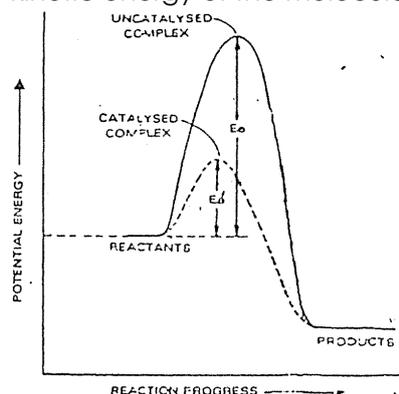
**6.7 ACTIVATION ENERGY AND CATALYSIS**

According to the collision theory, a reaction occurs by the collisions between the reactant molecules (or ions).



**Figure: 5** Mechanism of a molecular reaction

At **ordinary temperature**, the molecules **do not possess** enough energy and hence the **collisions are not effective**. However, when the temperature of the system is raised, the kinetic energy of the molecules increases.



**Figure: 6** Energy diagram of reaction with and without catalyst, showing clearly lowering of activation energy by catalyst

Thus larger numbers of effective collisions occur in the presence of the catalyst than would occur at the same temperature without the presence of the catalyst. In this way, the presence of the catalyst makes the reaction go faster, other conditions remaining the same.

But the molecules do not react unless they attain a minimum amount of energy. **The minimum amount of energy required to cause a chemical reaction is known as the Activation energy**. The activated molecules on collision first form an Activated Complex. As a result of breaking and forming of new bonds, the **activated complex** dissociates to yield product molecules.

When a **catalyst** is present, it **lowers the activation energy** of the reaction by providing a new pathway (mechanism).

## 6.8 THEORIES OF CATALYSIS

There are **two main theories** of catalysis

1. Intermediate compound formation theory
2. The adsorption theory.

In general, the **intermediate compound formation** theory applies to **homogeneous** catalytic reaction and the **adsorption theory** applies to **heterogeneous** catalytic reaction.

### 6.8.1 The intermediate compound formation theory

As already discussed **catalyst** functions by providing new pathway of **lower activation energy**. In **homogeneous** catalysis does so by forming an **intermediate compound** with one of the reactants. The highly reactive **intermediate** compound then reacts with the **second reactant** to yield the **product**, releasing the catalyst. Let us illustrate it by talking the general reaction

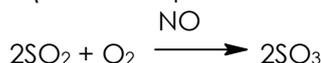


Where, C acts as a catalyst. The reaction proceeds through the reactions

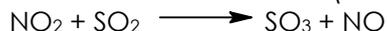
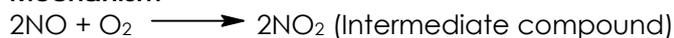


The activation energies of the reactions (2) and (3) are lower than the reaction (1). Hence the involvement of the catalyst in the formation of subsequent decomposition accelerates the rate of the reaction (1) which was originally very slow.

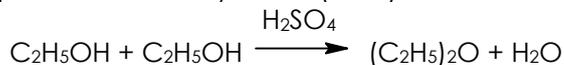
**Example: (1)** Catalytic oxidation of sulfur dioxide ( $\text{SO}_2$ ) in the presence of nitric oxide (NO) as catalyst. (Chamber process for sulfuric acid)



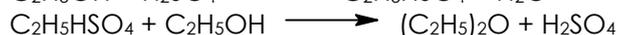
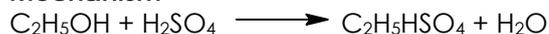
**Mechanism**



(2) Preparation of diethylether,  $(\text{C}_2\text{H}_5)_2\text{O}$  from ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) using sulfuric acid as catalyst.



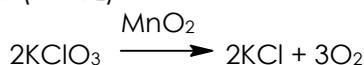
**Mechanism**



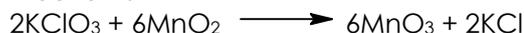
Ethyl hydrogen sulfate

(Intermediate compound)

(3) Thermal decomposition of potassium chlorate ( $\text{KClO}_3$ ) in the presence of manganese dioxide ( $\text{MnO}_2$ )



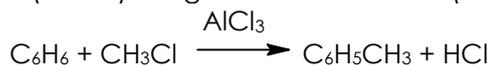
**Mechanism**



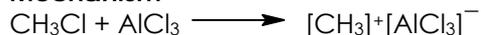
Intermediate compound



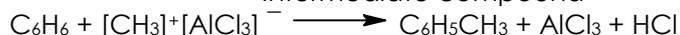
(4) Formation of methylbenzene,  $(\text{C}_6\text{H}_5\text{CH}_3)$  by reaction between benzene ( $\text{C}_6\text{H}_6$ ) and methyl chloride ( $\text{CH}_3\text{Cl}$ ) using aluminum chloride ( $\text{AlCl}_3$ ) as catalyst, (Friedel-Crafts reaction)



**Mechanism**



Intermediate compound



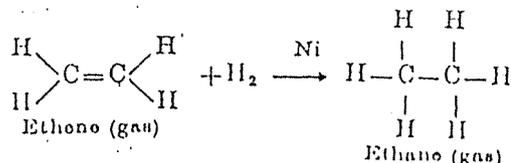
It may be noted that the actual isolation of intermediate compounds, which would prove their existence, is very difficult. As already stated, by their very nature, they are unstable. In general, the intermediate compounds suggested as being formed are usually possible rather than proved.

### 6.8.2 The adsorption theory

This theory explains the mechanism of a reaction between two gases catalyzed by a solid (heterogeneous or contact catalysis). Here the **catalyst** functions **by adsorption** of the reacting molecules on its surface

The adsorption theory is much the same as the intermediate compound formation theory. Here, the reactive intermediate compound or activated complex is formed on the catalyst surface itself.

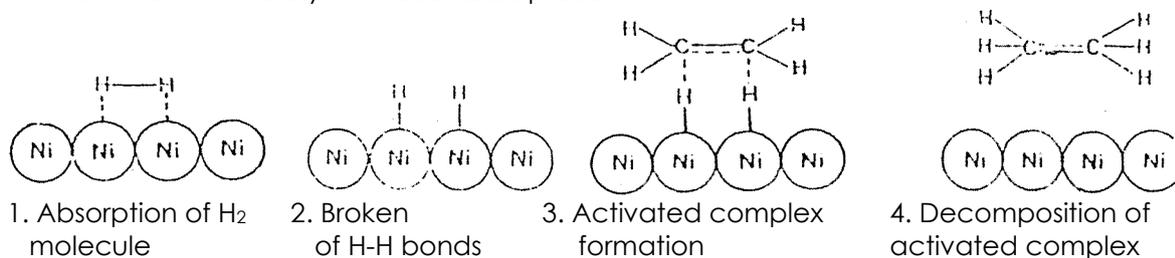
Let us illustrate the mechanism of contact catalysis by taking example of the hydrogenation of ethene in the presence of finely divided nickel as catalyst.



The **solid nickel catalyst** operates by the following steps:

#### (1) Adsorption of Hydrogen molecules

Hydrogen molecules strike the nickel surface and are held up there by Van der Waals forces or residual valence bonds of the nickel atoms, thus physical adsorption of hydrogen molecules on the catalyst surface takes place.



**Figure: 7** Mechanism of combination of Hydrogen and ethane on the surface of Ni catalyst

The adsorbed molecules of the reactants are crowded close together on the catalyst surface, whereas in the gaseous state they are far apart. This increased concentration of the reactants on the surface also accelerates the rate of the reaction (Law of mass action).

#### (2) The H-H bonds of the adsorbed hydrogen molecule are weakened and then broken

The H - H bond is smaller (0.74 Å) than Ni- Ni bond. Therefore the H-H bond of the hydrogen molecule adsorbed on nickel surface is stretched and weakened. The weakened bond breaks, separating the hydrogen atoms. The separated hydrogen atoms are held to the catalyst surface by chemical bonds (chemisorptions).

#### (3) Formation of the activated complex

The chemisorbed hydrogen atoms then attach themselves to the molecule of the second reactant, ethane by partial chemical bonds, thus forming an **activated complex**. This activated complex has lower energy than that required for the unchanged process. It has only a fleeting existence.

#### (4) Decomposition of the activated complex with release of the product from the catalyst surface

The unstable activation complex decomposes. The breaking of H-Ni bonds and establishing new bonds between H atoms and ethene molecule, results in the release (desorption) of the product (ethane) molecule. The freed catalyst surface is again available for further action.

### 6.9 ACTIVE CENTERS

Just like surface tension, the **catalyst surface** has **unbalanced chemical bonds** on it. The reactant gaseous molecules are **adsorbed** on the surface by those free bonds. This **accelerates** the rate of the reaction.

The distribution of **free bonds** on the **catalyst surface** is **not uniform**. These are **crowded** at the '**peaks**', '**cracks**' and '**corners**' of the **catalyst**. The catalytic activity due to

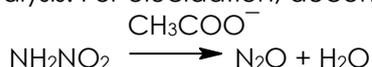


### 6.10.2 General acid base catalysis

More recently it has been found that:

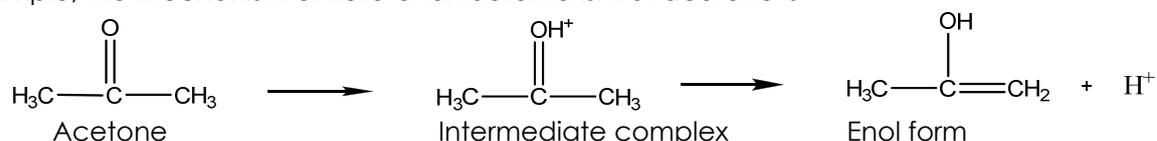
- Not only  $H^+$  ions but **all Bronsted acids** (proton donors) cause **acid catalysis**. Thus, the general acid catalysts are:  
 $H^+$ , undissociated acids ( $CH_3COOH$ ), cations of weak bases ( $NH_4^+$ ), and water ( $H_3O^+$ )
- Not only  $OH^-$  ions but **all Bronsted bases** (proton accepters) act as **base catalysts**. Thus the general base catalysts are:  
 $OH^-$ , un-dissociated bases, anions of weak acids ( $CH_3COO^-$ ) and water ( $H_2O$ )

The catalysis brought about by general acids and bases is termed general acid-base catalysis. For elucidation, decomposition of nitramide is also catalyzed by acetate ions



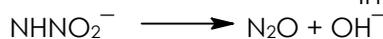
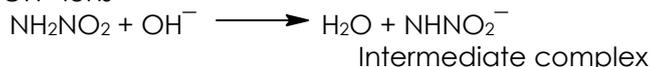
### 6.10.3 Mechanism of acid base catalysis

(a) **In acid catalysis:** the  $H^+$  (or a proton donated by bronsted acid) forms an intermediate complex with the reactant, which then reacts to give back the proton. For example, the mechanism of keto-enol tautomerism of acetone is

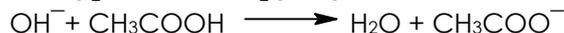
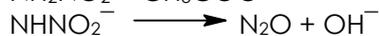
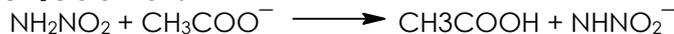


(b) **In base catalysis:** the  $OH^-$  ion (or any bronsted base) accepts a proton from the reactant to form an intermediate complex, which then reacts or decomposes to regenerate the  $OH^-$  (or Bronsted base). For example, the decomposition of nitramide by  $OH^-$  ions and  $CH_3COO^-$  ions may be explained as follows:

(1) By  $OH^-$  ions



(2) By  $CH_3COO^-$  ions



## 6.11 ENZYME CATALYSIS

Numerous organic reactions are taking place in the body of animals and plants to maintain the life process. These reactions being shown are remarkably catalyzed by the organic compounds known as **Enzymes**. All enzymes have been found to be complex protein molecule. Thus:

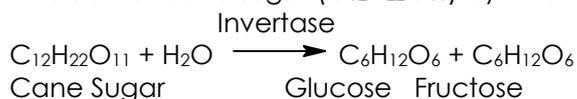
**Enzymes are protein molecules which act as catalysts to speed up organic reactions in living cells. The catalysis brought about by enzymes is known as Enzyme catalysis.**

Each enzyme is produced in a particular living cell to catalyze a reaction occurring in that cell. Many enzymes have been identified and obtained in pure crystalline state from the cells to which they belong. However the unit enzyme was prepared by synthesis in the laboratory in 1969

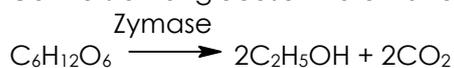
### 6.11.1 Examples of enzyme catalysis

Some common examples of the biochemical reactions catalyzed by enzymes are :

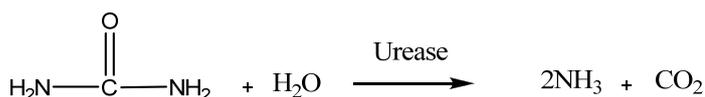
(1) Inversion of cane sugar ( $C_{12}H_{22}O_{11}$ ) by Invertase present in yeast,



(2) Conversion of glucose into ethanol by Zymase present in yeast,

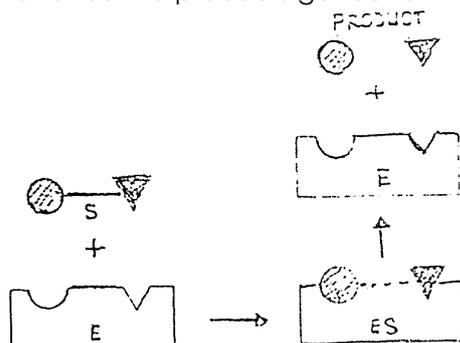


(3) Hydrolysis of Urea ( $H_2N-CO-NH_2$ ) by urease present in soybean



### 6.11.2 Mechanism of enzyme catalysis

The long chains of the **enzyme** (protein) molecule are **colloidal** on each other to make a rigid colloidal particle with **cavities** on its surface. These cavities, which are of characteristic shape and **abound** in **active groups** (NH<sub>2</sub>, COOH, SH, OH) are termed **active centers**. The molecule of substrate, which has complementary shape, fit into these cavities just as key fits into a lock (lock and key theory). By virtue of the presence of active groups, the enzyme forms an activated complex with the substrate which at once decomposes to yield the products. Thus the substrate molecule enters the cavities, forms complex and reacts and at once the products get out of the cavities.



**Figure: 10** Mechanism of enzyme catalysis

Michaelis and Menten (1913) proposed the following mechanism for enzyme catalysis (See figure)



Where, E = enzyme; S = substrate (reactant)

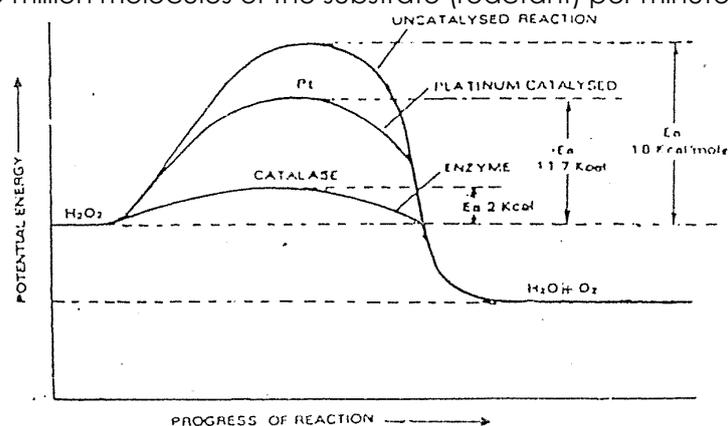
ES = activated complex; P = products.

### 6.11.3 Characteristics of enzyme catalysis

In general, **enzymes** behave like **inorganic heterogeneous catalysts**. However, they are unique in their efficiency and high degree of specificity. Some more **important features** of **enzyme catalysis** are listed below.

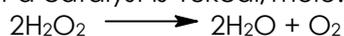
#### (1) Enzymes are the most efficient catalysts known

The enzyme catalyzed reactions proceed at fantastic high rates in comparison to those catalyzed by inorganic substances. Thus one molecule of an enzyme may transform one million molecules of the substrate (reactant) per minute.



**Figure: 11** Enzyme lowers the activation energy

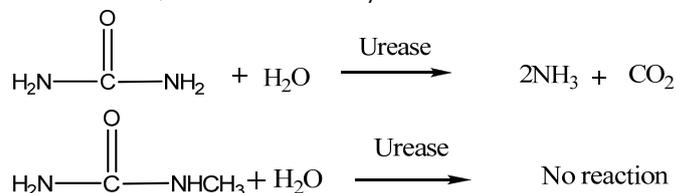
Like inorganic catalysis, enzymes function by lowering the activation energy of a reaction. For example, the activation energy of the decomposition of hydrogen peroxide without a catalyst is 18kcal/mole.



With colloidal platinum (inorganic catalyst), the activation energy is lowered by 11.7 kcal/mole. The enzyme catalyze lowers the activation energy of the same reaction to less than 2 kcal/mole.

**(2) Enzyme catalysis is marked by absolute specificity**

An enzyme as a rule catalyses just one reaction with a particular substance. For example, urease (an enzyme derived from soya bean) catalyses the hydrolysis of urea and no other amide, not even methylurea.

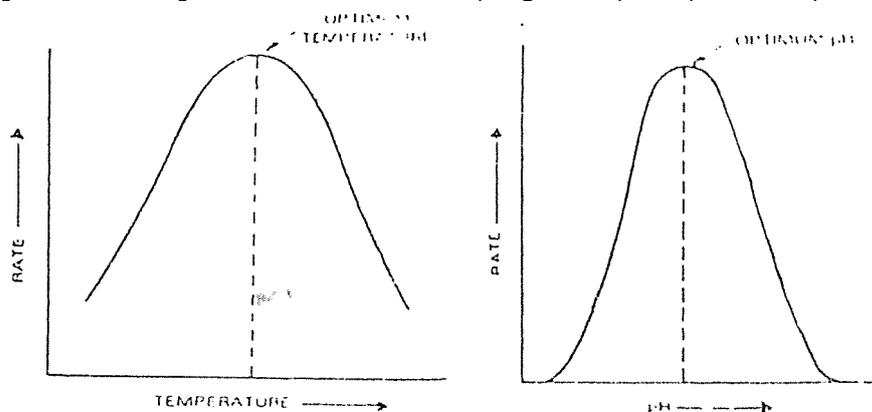


Enzyme catalyzed reactions are often marked by absolute specificity. Thus where a compound can exist in optically active isomers (identical in every respect except the space arrangement of groups) an enzyme which can act on one of the isomer is unable to act on the other. For example, the enzyme present in ordinary mould (*Penicillium glaucum*) when added to dl-mixture of tartaric acid decomposes the d-form only, leaving the l-form behind.

**(3) The rate of enzyme-catalyzed reaction is maximum at the optimum temperature**

The rate of enzyme catalyzed reaction is increased with the use of temperature but up to a certain point. There after the enzyme is denatured as its protein attendance is gradually destroyed. Thus the rate of reaction eventually drops and eventually becomes zero when the enzyme is completely destroyed the rate of an enzyme reaction with raising of temperature gives a bell-shaped curve. The temperature at which the reaction rate is maximum is called as optimum temperature.

For Example: the optimum temperature of enzyme reaction occurring in human body as in figure. As much **higher temperatures** all **physiological** reactions will **cease** due to **loss of enzymatic activity**. This is one reason why high body temperature (fever) is very dangerous.



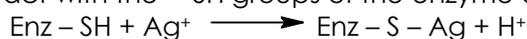
**Figure: 12** Variation of rate of an enzyme catalyzed reaction with Increase of temperature and pH

**(4) Rate of enzyme catalyzed reaction is maximum at the optimum pH**

The rate of an enzyme-catalyzed reaction varies with pH of the system. The rate passes through a maximum at a particular pH, known as the optimum pH. The enzyme activity is lower at other values of pH. Thus many enzymes of the body function best at pH of about 7.4, the pH of the blood and body fluids.

**(5) Enzymes are markedly inhibited or poisoned**

The catalytic **activity** of an enzyme is often reduced (inhibited) or completely **destroyed** (poisoned) by **addition of other substances**. These inhibitors or poisons interact with the active functional groups on the enzyme surface. For example, heavy metal ions ( $\text{Ag}^+$ ,  $\text{Hg}^+$ ) react with the  $-\text{SH}$  groups of the enzyme and poison it.



The physiological activity of many drugs is related to their action as enzyme inhibitors in the body. Thus sulfa drugs, penicillin and streptomycin inhibit the action of several bacteria

and have proved effective in curing pneumonia, dysentery, cholera, and many other infections.

**(6) Catalytic activity of enzymes is greatly enhanced by the presence of Activators or Coenzymes**

Activators are **metal ions**  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  etc., which get weakly bonded to enzyme molecules and **promote** their catalytic action. Thus it has been found that the addition of sodium chloride ( $\text{Na}^+$ ) makes amylose catalytically very active.

Often, a small non-protein (vitamin) termed a coenzyme when present along with an enzyme, promotes the catalytic activity of the latter.

**6.12 SOME INDUSTRIALLY IMPORTANT CATALYTIC PROCESSES AND APPLICATIONS**

**(1) Synthesis of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$**

- Beginning Fe, today  $\text{Fe}^+$  promoters well understood mechanism.
- Dissociation of N followed by that of  $\text{H}_2$
- High temperature and high pressure.
- Catalytic cycle turn over more than a billion at each site before it is replaced.
- Catalyst gives products worth 2000 times its cost during its life

**(2) Catalytic reforming of naphtha**

- Production of high-octane gasoline (petrol)
- Small particles of Pt with second metal such as rhenium or iridium/acidic Metal oxide.
- Expensive but robust bimetallic catalyst
- Reactivation after long term use.
- Practically all metal atoms exposed to reactants.

**EXAMPLES**

**(3) Biomimetic industrial catalysts**

- Imitating the enzymes to produce optically active stereo isomer.  
e.g. Pharmaceutical molecules
- L-Dopa for Parkinson's disease (Left-handed active, right handed inactive)  
Monsanto patent (1974) for selective synthesis of L—Dopa
- Heralded, as revolutionary discovery

**(4) Protection of Environment**

- Catalytic converters for automobile exhaust introduced in USA (1974).
- Three metals of platinum group to control emissions of CO, NO<sub>x</sub> and unburnt hydrocarbons.
- Complex network of catalytic reactions.

**(5) Immobilized enzyme as industrial catalyst**

Fructose, Sweetener and choice

- Catalyst glucose isomerase - streptomyces (soil-dwelling bacterium) an enzyme.
- Enzyme, a protein molecule - long chain of amino acids (100s of 1000s units).
- Several crevices in protein
- Enzyme on ceramic coated with special polymer.
- Fructose production very efficient
- 1 Kg. of catalyst coated ceramic produces 28.5 ton to 36 ton. Fructose (it life)
- Process converts the watery honey-coloured syrup (95% glucose), which is a byproduct of wet-milling process in corn - starch production.
- 42% fructose syrup "Corn - sweetener"
- Sweetening scale: Sucrose (100), Fructose (173), Glucose (74) - unsatisfactory
- Glucose recycled. Product 90% Fructose. Sold as 55% solution.
- Pepsi and cock (Soft drinks)

**(6) Catalytic cracking**

- Large HC molecules into smaller ones.
- Inefficient cracking leads to methane, ethane and high molecular weight residue.
- Thermal cracking most primitive

- 1936 - Acid washed natural clays
- 1940s - Amorphous  $\text{SiO}_2 - \text{Al}_2\text{O}_3$
- 1950s early 1960s - Zeolites (Mobil)
- All refineries - Y- Zeolite and in some instances ZSM - 5.
- 1% shift in product selectivity leads to savings of 400 million barrels per year (\$8 billion at £ 20/ Bbl.) (US)
- Reduction in oil imports by more than 22 million barrels of crude per year.

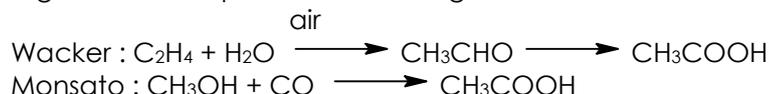
#### (7) Production of chemicals

For existing products

- Major emphasis placed on greater advances rather than marginal gains.
- Large volume bulk chemicals.
- Shift to a lower-cost feedstock or to a simpler, less capital intensive route.

#### Lower Cost Feed stocks

- 60 – 70% of total product cost, due to feedstock. --- Cheaper feedstock. e.g. Monsanto process for making acetic acid via MeOH carbonylation,



#### CURRENT THRUST

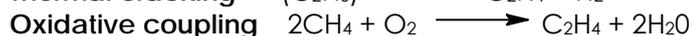
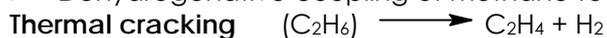
- (1) Substituted alkanes (Ethane, propane, butane) for the corresponding olefins, and convert methane to olefins or aromatics (price -difference Rs.10/kg.)

##### Example

- Maleic anhydride monomer for specialty plastics,
- Shift from high-priced toxic benzene to butenes to lower-cost butane.
- Due to vanadyl phosphate (Chevron).
- Novel catalyst by Du Pont (1990s).

- (2) **Catalytic oxidative coupling of methane to petro-chemicals and liquid fuels.**

- Methane → Ethylene
- Methane → aromatics
- Oxidative methylation of toluene to ethylbenzene and styrene.
- Oxidative methylation of propylene to  $\text{C}_4$  olefins.
- Dehydrogenative coupling of methane to aromatics.



##### **LPG to aromatics**

- Relative abundance of LPG (propane and butane)
- Zeolitic conversion (B.P. and UOP)
- Aromatics yield 65% (95% B, T, X)

- (3) **Single step ammoxidation** (B.P.chemicals) Propane→Acrylonitrile

- (4) **Gasoline octane boosters**

MTBE, ETBE, TAME

- Alkane dehydrogenation to produce isobutylene and propylene.
- Natural gas.

- (5) **Catalytic dehydrogenation of paraffin**

- Production of linear olefins,  $\text{C}_{10}-\text{C}_{17}$  for manufacture of biodegradable detergents
- $\text{C}_{10}-\text{C}_{14}$  olefins for LAB.
- $\text{C}_{14}-\text{C}_{17}$  for detergent alcohols.
- Heavy olefins for lube oils.
- Replacement of HF or  $\text{AlCl}_3$  in LAB

#### **New catalytic oxidation processes**

- HC oxidation, low selectivity.
- Partial oxidation desired but  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  are produced.
- Highly capital intensive.

**One stage oxidation of CH<sub>4</sub>**

- MeOH /of higher alkanes→ alcohols / of propylane → propylene oxide / of benzene → phenol

**NEW PRODUCT**

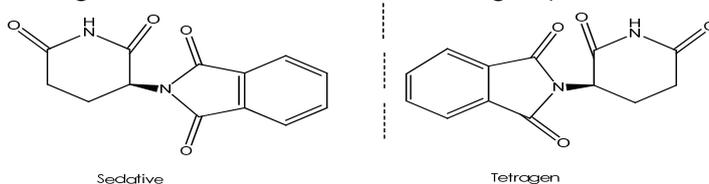
- Polymers/ pharmaceuticals and biotech.

**Polymers**

- Raw Polymers \$ 30 billion (USA)
- Environmental issues, availability and cost of feedstock
- New and improved polymers (polyolefins)
- Polyolefins evolved out of ziegler-natta catalyst of 1950s.
- New: Syndiotactic polypropylene true thermoplastic elastomers (e.g. Propylene-elastomers polypropylene resin, propylene block co-polymers).
- Incorporation of polar monomers into various polyolefins classes.
- Cyclic olefins, e.g. trans-poly(octenamol)
- Functionalised monomers, new and existing monomers via biomass, coal or C<sub>1</sub> Chemistry.
- Genetic engineering of enzymatic catalysts
- None—phosgene routes to diisocyanates.

**Pharmaceuticals**

- 1990s, a decade of chirality
- Wrong enantiomer of a racemic drug represents a "medical pollutant"



- R isomer is sedative. S- powerful teratogen
- Asymmetric catalysis, powerful and unique advantages.

**Biologically derived products**

- Biotechnology and enzyme catalysis
- Genetically engineered microorganisms in synthesizing rate and valuable peptides used in human therapeutics
- Molecular biology to improve enzymes, enzymatic reaction in aqueous solution at moderate temperature, pressure and pH
- Environment friendly.
- Genetically engineered Escherichia coli to synthesis D-biotin from glucose.
- Vitamin C precursor from glucose
- Enzymes: Acrylonitrile to amide (Japan).

**Enzyme catalysis**

- Synthesis of monosodium glutamate
- L-tryptophan and phenylalanine
- Benzene to polyphenylene (ICI)
- Biodegradable poly (β-hydroxybutyrate by microorganism)

**Production of fuels****1) Eco-friendly petrol**

- New cracking catalysts: to produce motor fuels.

**2) Oxygenates**

- MTBE/ ETBE
- Alcohols, ethers, carbonates/acetates (150,000 b/d MTBE, EDH to etrol in USA)

**3) Methanol to CO and H (New Fuel)**

- Cu or Zn based catalysis:

**Environment protection**

- Replacement of CFCs (1.25 billion kg/year usage).
- Refrigerants (30%)/ from blowing agents (28%)
- Industrial solvents and cleaners (19%)

**Montreal protocol**

- Phasing out CFCs by 2000.
- Hydrogenated CFC

**Biodegradation of organic waste**

- Enzymes

**6.13 CATALYST CHARACTERIZATION**

Techniques	Acronym	Information
Low energy electron diffraction	LEED	2-D structure and registry with metals
Auger electron spectroscopy	AES	Elemental analysis
X-ray photoelectron spectroscopy	XPS	Elemental analysis and valance state
Ion scattering spectroscopy	ISS	Elemental analysis
UV photoelectron spectroscopy	UPS	Electronic structure
Electron energy loss spectroscopy	EELS	Molecular structure
Infrared spectroscopy	IRS	Molecular structure
Laser raman spectroscopy	LRS	Molecular structure
X-ray diffraction	XRD	Bulk crystal structure
Extended X-ray absorption fine structure	EXAFS	Bond distance and co-ordination
Transmission electron microscopy	TEM	Crystal size, shape, morphology and structure
Scanning TEM	STEM	Microstructure and composition
Scanning tunneling microscopy	STM	Microstructure
UV spectroscopy	UV	Electronic state
Mossbauer spectroscopy	--	Ionic state