

2. Catalyst (4 Teaching hours)

2.1. Introduction

2.2. Action of Catalyst (Catalytic Promoters and Catalytic Poisons)

2.3. Characteristics of Catalyst

2.4. Types of Catalysis

a) Homogeneous Catalysis

b) Heterogeneous Catalysis

2.5. Theories of Catalysis

a) Intermediate Compound Formation Theory

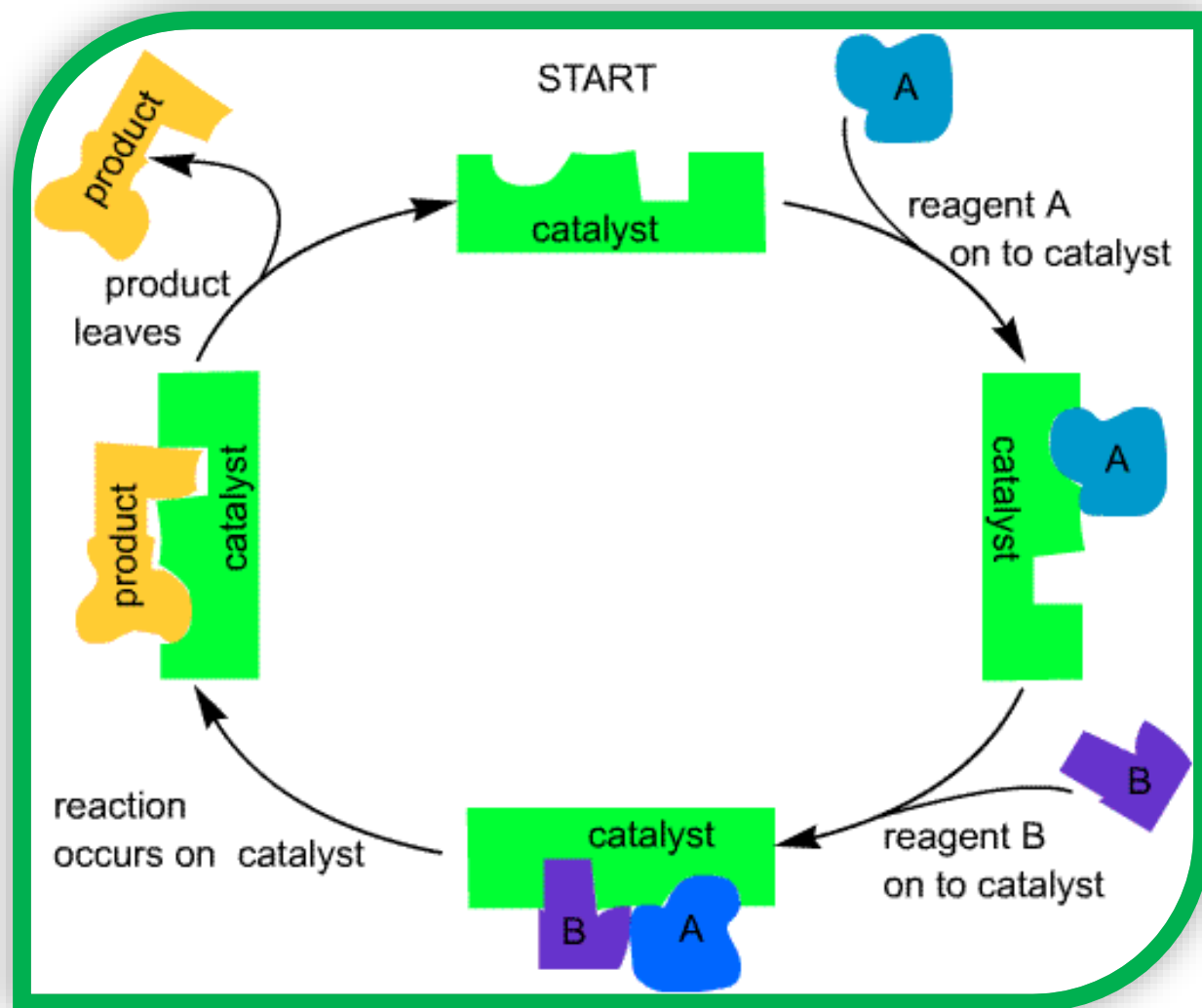
b) Adsorption Theory

2.6. Industrial Applications of Catalysts – Criteria of Choosing Catalyst for Industry and some industrial Processes Using Catalyst.

Introduction

The term catalysis (*from the Greek kata-, “down,” and lyein, “loosen”*) was first employed by the great Swedish chemist **Jöns Jacob Berzelius** in 1835. Catalyst is the substance which *modifies the rate of chemical reaction by altering the activation energy barrier (path of the reaction) without itself undergoing any change in mass and composition* at the end of reaction.

Catalysis is the phenomenon of *altering the path of reaction so as to bring change in reaction rate*.



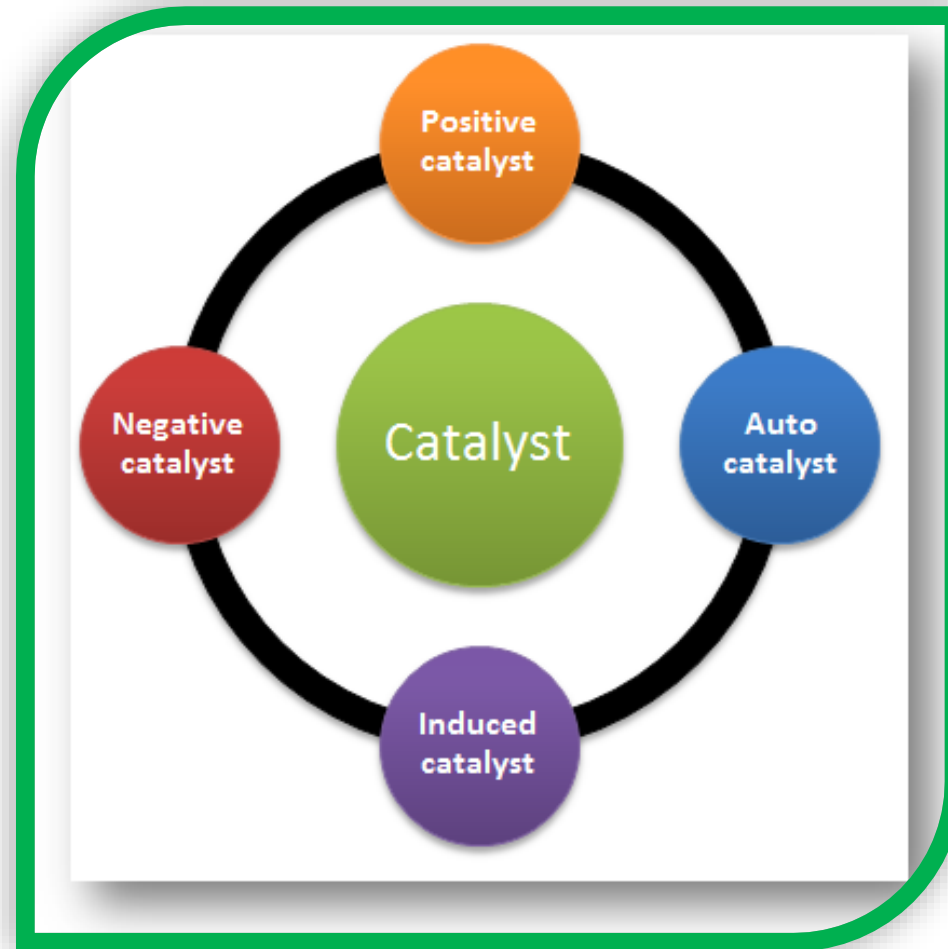
Types of Catalyst

Positive catalyst

Negative catalyst

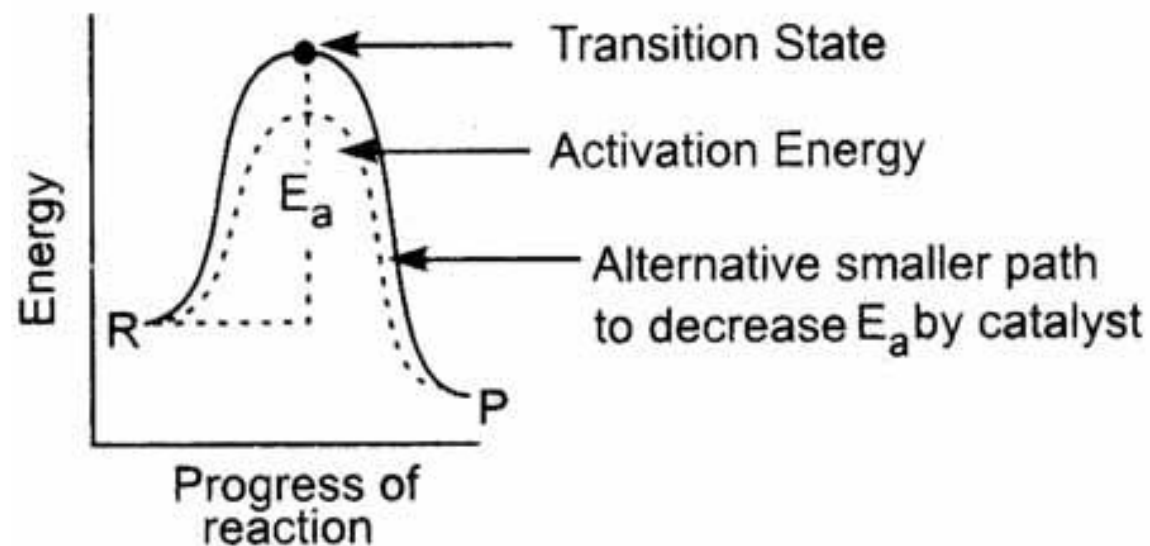
Auto-catalyst

Induced Catalyst



Positive catalyst

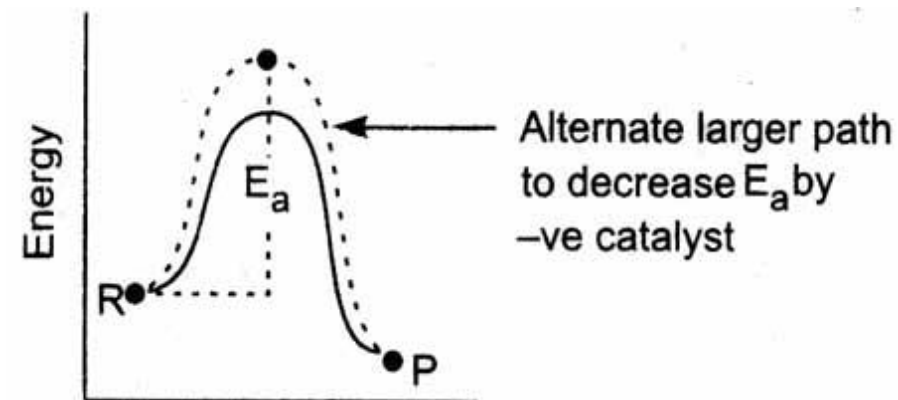
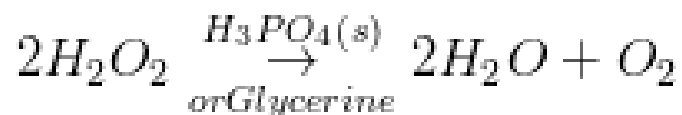
A catalyst which *enhances the rate of reaction* is called positive catalyst. Such catalyst *decreases activation energy barrier by following an alternative path so rate of reaction gets increased*



Negative catalyst

A catalyst which *suppress the rate of reaction* is called negative catalyst. Such catalyst *increases activation energy barrier by following an alternative path so rate of reaction gets decreased*

It is because a -ve catalyst increase activation energy by taking a longer alternative path.



Acetanilide also acts as -ve catalyst in decomposition of H_2O_2

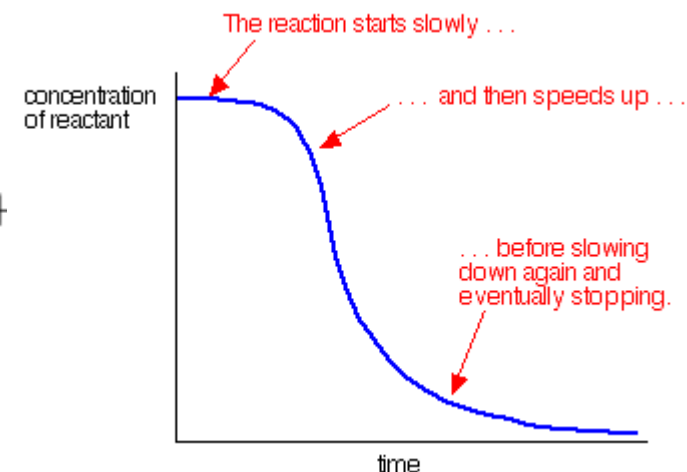
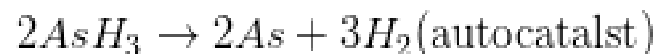
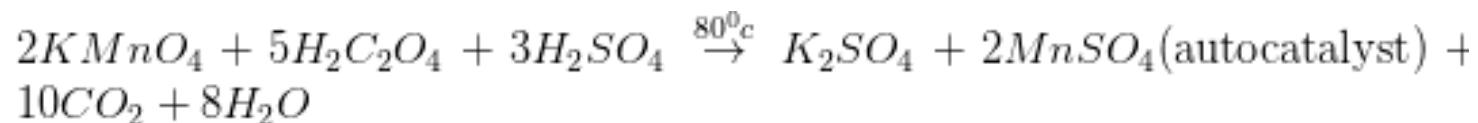
T.E.L (Tetra Ethyl Lead) an ant knocking substance is added to petrol to decrease the ignition of petrol vapours.

Here C_2H_5OH acts as -ve catalyst to slow the oxidation



Auto-catalyst

When one of the *products formed in the reaction acts as a catalyst* is known as auto-catalyst.



In this reaction NO_2^- acts as auto catalyst which is formed as a side reaction:

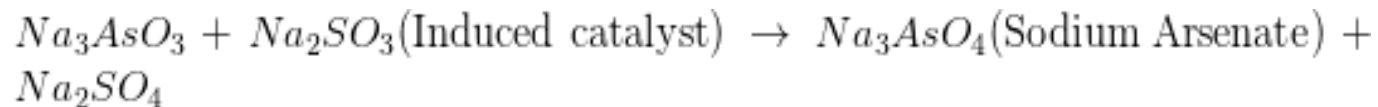


Auto catalysis reaction starts slowly in the beginning but as auto catalyst is formed rate of reaction starts increasing.

Induced Catalyst

The *substance which influences the speed of other reaction, which is not possible under ordinary conditions*, is known as induced catalyst.

Sodium sulphite solution readily oxidises in air, but sodium arsenite solution does not oxidise by passing air in the solution. When both these solutions are mixed and air is passed then both the substances get oxidised.

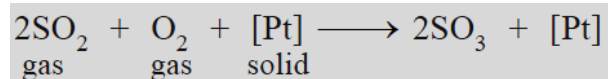


Heterogeneous Catalysis

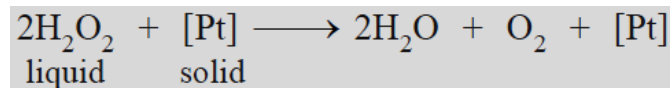
In chemistry, heterogeneous catalysis refers to *the form of catalysis where the phase of the catalyst differs from that of the reactants*. The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases or liquids. Heterogeneous catalysis is of paramount importance in many areas of the chemical and energy industries. Heterogeneous catalysis has attracted *Nobel prizes for Fritz Haber and Carl Bosch in 1918, Irving Langmuir in 1932, and Gerhard Ertl in 2007*.

The process is *also 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 a gauze. This form of catalysis has great industrial importance. Examples of Heterogeneous Catalysis:

- ❖ Heterogeneous catalysis with gaseous reactants (Contact catalysis): Combination of sulphur dioxide (SO₂) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V₂O₅, (*Contact Process for Sulphuric acid*).



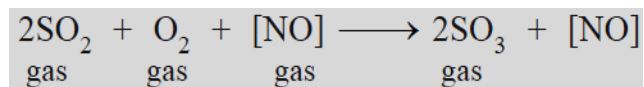
- ❖ Heterogeneous catalysis with liquid reactants: The decomposition of aqueous solutions of hydrogen peroxide (H₂O₂) is catalyzed by manganese dioxide (MnO₂) or platinum in colloidal form,



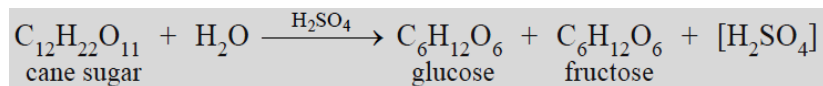
Homogeneous Catalysis

In chemistry, homogeneous catalysis is a sequence of reactions that involve a *catalyst in the same phase as the reactants*. Phases here refer to solid, liquid and gas. Most commonly, a *homogeneous catalyst is co-dissolved in a solvent with the reactants*.

Examples of Homogeneous Catalysis in Gas Phase: Oxidation of sulphur dioxide (SO₂) to sulphur trioxide (SO₃) with nitric oxide (NO) as catalyst,



Examples of Homogeneous Catalysis in Solution Phase: Many reactions in solutions are catalyzed by acids (H⁺) and bases (OH⁻). Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst,



Major differences between homogeneous and heterogeneous catalysts

	Homogeneous	Heterogeneous
Form	Soluble metal complexes, usually mononuclear	Metals, usually supported, or metal oxides
Active site	well-defined, discrete molecules	poorly defined
Phase	Liquid	Gas/solid
Temperature	Low (<250°C)	High (250 – 500°C)
Activity	Moderate	High
Selectivity	High	Low
Diffusion	Facile	Can be very important
Heat transfer	Facile	Can be problematic
Product separation	Generally problematic	Facile
Catalyst recycle	Expensive	Simple
Catalyst modification	Easy	Difficult
Reaction mechanisms	Reasonably well understood	Poorly understood

Characteristics of Catalysis

The following are the characteristics which are common to most of catalytic reactions.

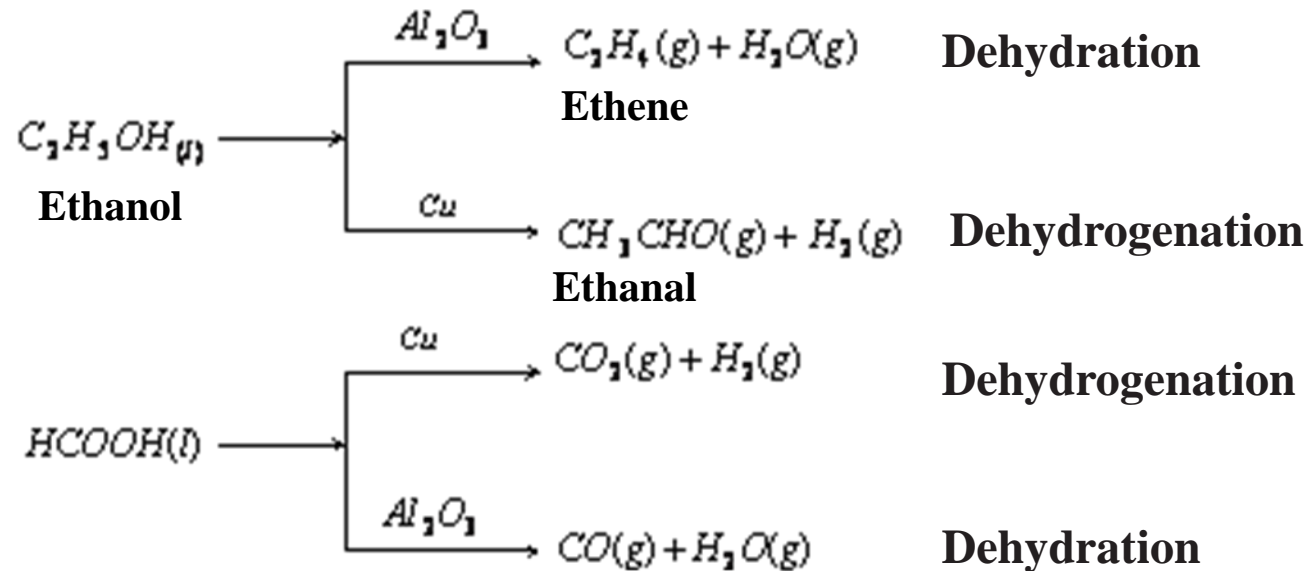
1. A catalyst remains *unchanged in mass and chemical composition* at the end of the reaction.
2. A small quantity of the catalyst *is generally sufficient to catalyses almost unlimited reactions*. For example,
 - a) In the decomposition of hydrogen peroxide, one gram of colloidal platinum can catalyses litres of hydrogen peroxide
 - b) In Friedel craft's reaction, anhydrous aluminium chloride is required in relatively large amount to the extent of 30% of the mass of benzene



3. The catalyst *can not initiate the reaction*: The function of the catalyst is to *alter the speed of the reaction rather than to start it*.

4. The catalyst is *generally specific in nature*: A substance, which acts as a catalyst for a particular reaction, fails to catalyse the other reaction, different catalysts for the same reactant may form different products.

Examples :



5. The catalyst *can not change the position of equilibrium* : The catalyst catalyses both forward and backward reactions to the same extent in a reversible reaction and thus has no effect on the equilibrium constant.

Catalytic Promoters

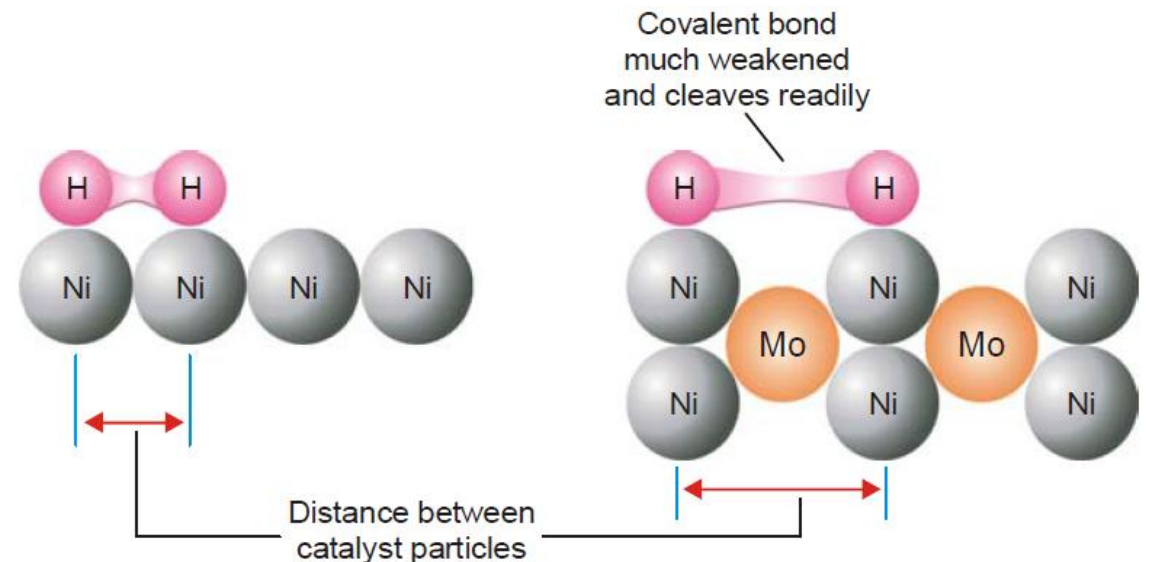
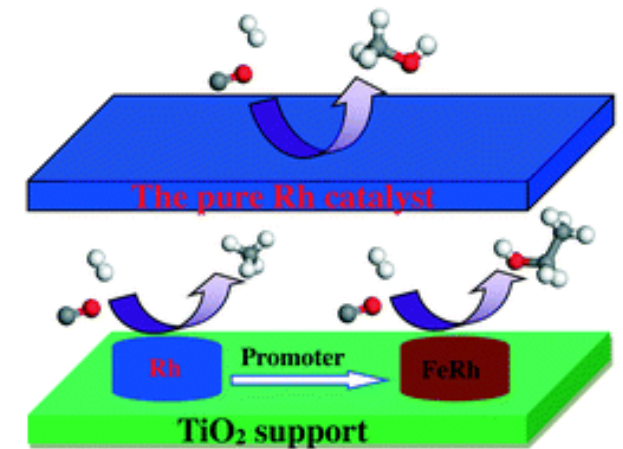
Substances which *themselves are not catalysts, but are mixed in small quantities with the catalysts to enhance the catalytic efficiency* are called as promoters or activators. For example:

- A classic example of promoters is alkali metals in Mittasch-type iron or ruthenium based catalysts for ammonia synthesis from nitrogen and hydrogen (the Haber–Bosch process).
- In the manufacture of methyl alcohol from water gas, chromic oxide is used as a promoter with catalyst zinc oxide.

Explanation of Promotion Action

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 absorbed molecules of the reactant (say H_2) are further weakened and cleaved. This makes the reaction go faster.
- (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.



Catalytic Poisoning

Substances which, *in their presence, reduce the catalytic activity of a catalyst* are called catalytic poisons. poisons are chemical species that *extinguish the catalytic activity of the catalyst when they are present on the catalyst surface*.

Well-known examples:

- sulfur poisoning catalysts used in petroleum refining
- carbon monoxide poisoning platinum-based electro-catalysts in proton-exchanged membrane fuel cells. Catalysts are not consumed in chemical reactions, they can be used repeatedly over an indefinite period of time.

Explanation of Catalytic Poisoning

- **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 As_2O_3 or CO appears to be of this kind.
- **The catalyst may combine chemically with the impurity:** The poisoning of iron catalyst by H_2S falls in this class.

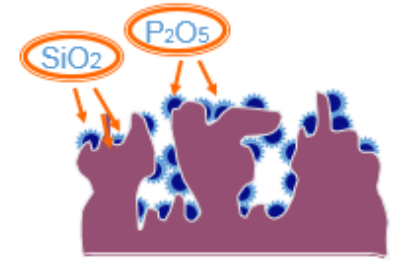


Non-Poisoned Active Site

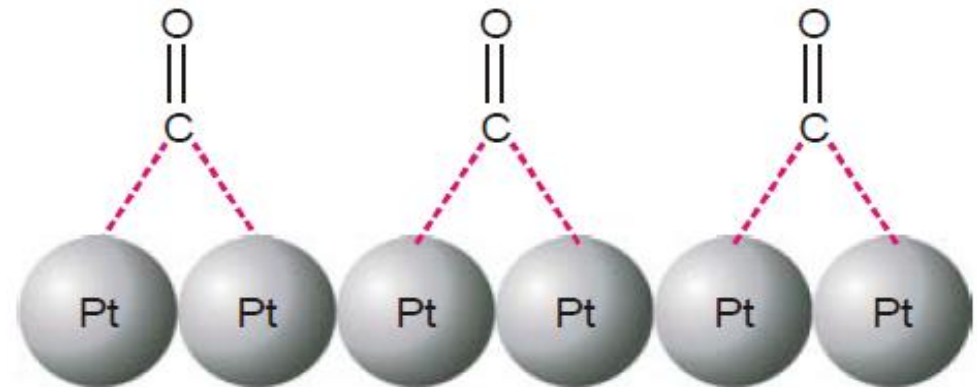


Non-Poisoned Catalyst Surface

Poisoned Active Site



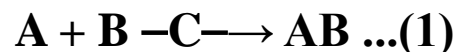
Poisoned Catalyst Surface



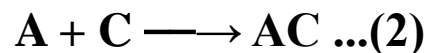
THEORIES OF CATALYSIS

1. The Intermediate Compound Formation Theory:

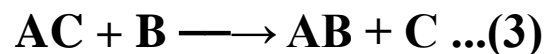
As already discussed a catalyst functions by providing a new pathway of lower activation energy. In homogeneous catalysis, it does so by forming an intermediate compound with one of the reactants. The highly reactive intermediate compound then reacts with the second reactant to yield the product, releasing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



where C acts as catalyst. The reaction proceeds through the reactions :



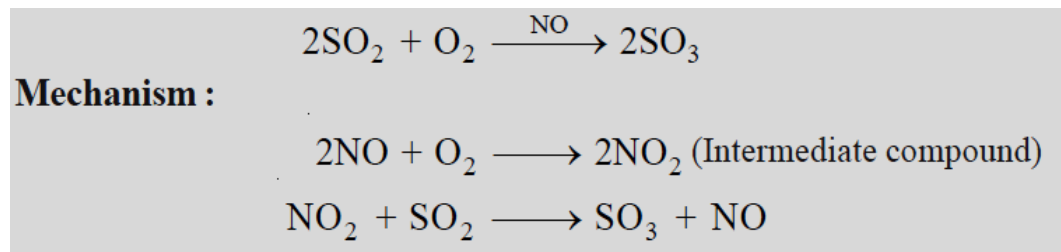
Intermediate



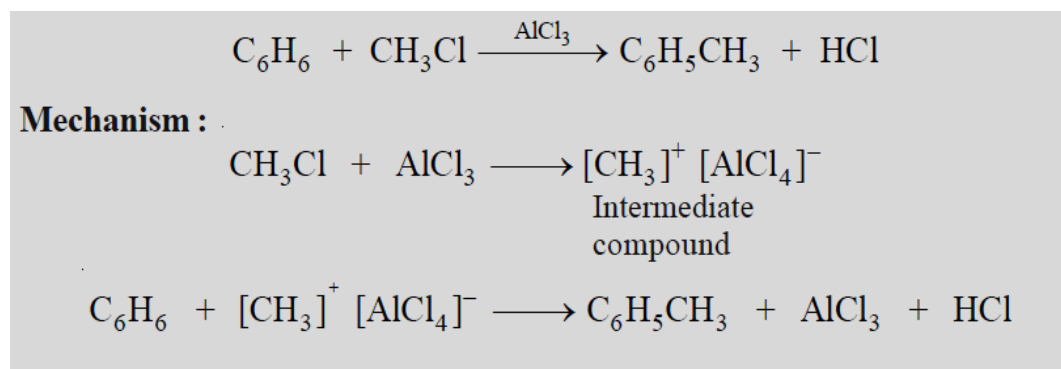
The activation energies of the reactions (2) and (3) are lower than that of the reaction (1) Hence the involvement of the catalyst in the formation of the intermediate compound and its subsequent decomposition, accelerates the rate of the reaction (1) which was originally very slow.

General examples are given below:

Example 1. Catalytic oxidation of sulphur dioxide (SO₂) in the presence of nitric oxide (NO) as catalyst. (Chamber Process of Sulphuric acid)



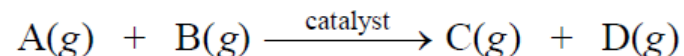
Example 2. Formation of methylbenzene, C₆H₅CH₃ by reaction between benzene, C₆H₆, and methyl chloride, CH₃Cl, using aluminium chloride AlCl₃, as catalyst (Friedel-Crafts reaction),



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 plausible rather than proved.

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. Generally speaking, four steps can be put forward for heterogeneous catalysis. For example, if the reaction is :



Step 1. Adsorption of Reactant molecules

The reactant molecules A and B strike the catalyst surface. They are held up at the surface by weak van der Waals forces (Physical adsorption) or by partial chemical bonds (Chemisorption).

Step 2. Formation of Activated complex

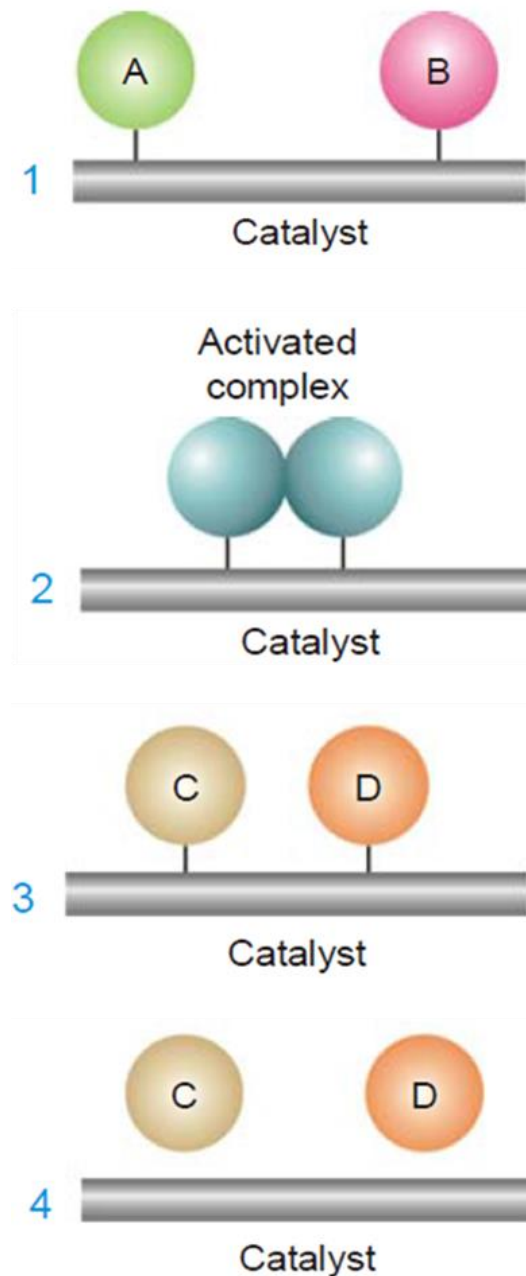
The particles of the reactants adjacent to one another join to form an intermediate complex (A – B). The activated complex is unstable. It has only fleeting existence.

Step 3. Decomposition of Activated complex

The activated complex breaks to form the products C and D. The separated particles of the products hold to the catalyst surface by partial chemical bonds.

Step 4. Desorption of Products

The particles of the products are desorbed or released from the surface. They are stable and can lead an independent existence. The mechanism of contact catalysis may vary in details, depending on the nature of the reactants.



HYDROGENATION OF ETHENE (ETHYLENE) IN PRESENCE OF NICKEL

Step 1. Adsorption of Hydrogen molecules

Hydrogen molecules are adsorbed on the nickel surface due to the residual valence bonds of the nickel atoms.

Step. 2 H–H Bonds are broken

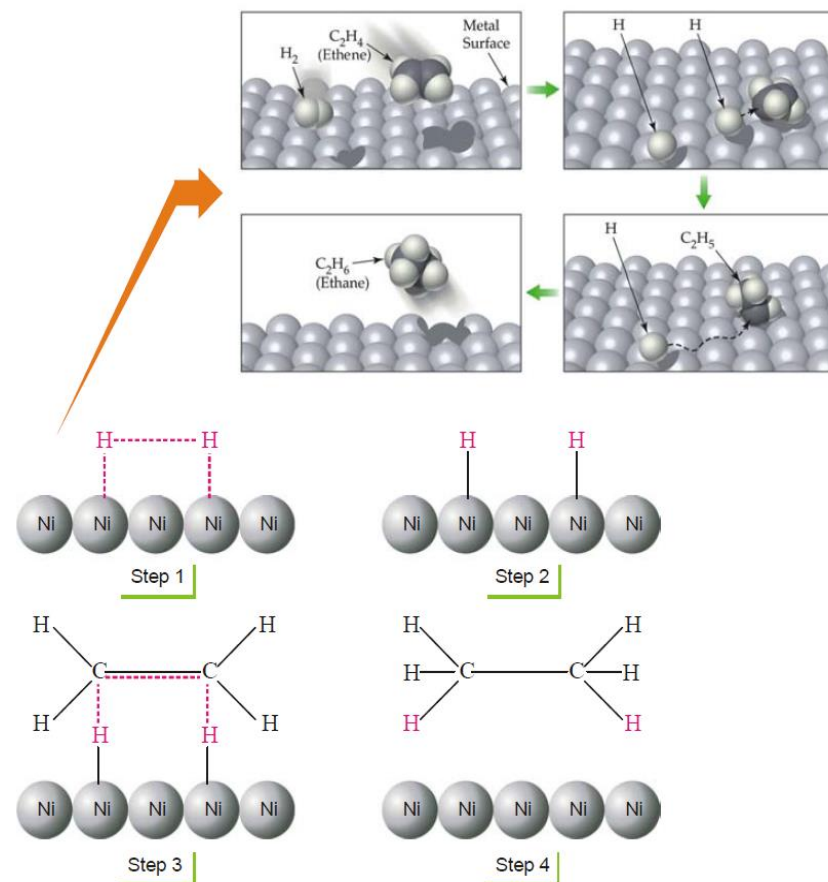
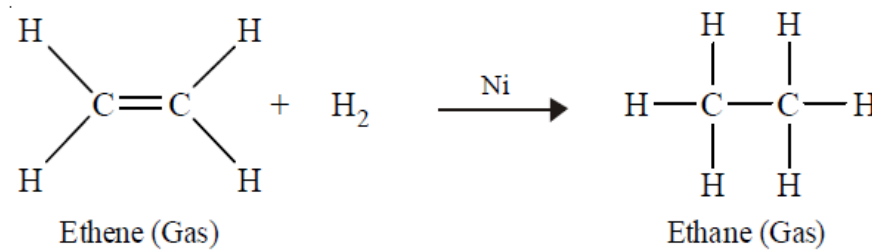
The H–H bond is smaller (0.74\AA) than Ni–Ni bond. Therefore, the H–H bond of the adsorbed hydrogen molecule is stretched and weakened. The weakened bond breaks, separating the hydrogen atoms. The separated hydrogen atoms are held to the nickel surface by chemical bonds.

Step 3. Formation of the Activated complex

The chemisorbed hydrogen atoms then attach to ethene molecule by partial chemical bonds. The unstable activated complex is thus formed.

Step 4. Decomposition of the Activated complex and desorption of ethane molecules

The unstable activated complex decomposes to release ethane molecules. The freed catalyst surface is again available for further action.



Industrial Catalyst:

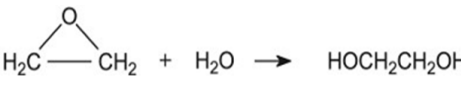
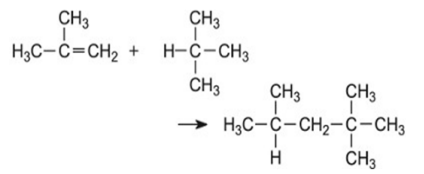
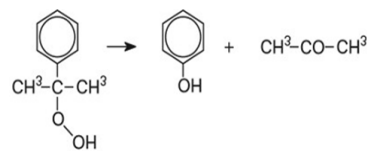
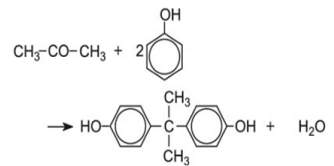
In the chemical industry and industrial research, catalysis play an important role. Different catalysts are in constant development to fulfil economic, political and environmental demands. When using a catalyst, it is possible to replace a polluting chemical reaction with a more environmentally friendly alternative.

Criteria for choosing a catalyst for industrial application:

To be successful the catalyst must allow the reaction to proceed at a suitable rate under conditions that are economically desirable, at as low a temperature and pressure as possible. It must also be long lasting.

- It must be *economical, accessible, green and regenerative*.
- It must be *stable in given set of reaction conditions*.
- It must be *specific/selective towards the reaction so as to get desired product*.

Some large-scale industrial processes incorporating Homogeneous catalysts are listed below:

Manufacture	Catalyst	Equation
Ethane-1,2-diol	Sulfuric acid	
2,2,4-Trimethylpentane (iso-octane)	Hydrogen fluoride	
Phenol and propanone	Sulfuric acid	
Bisphenol A	Sulfuric acid	

Homogeneous catalysts are less frequently used in industry than heterogeneous catalysts as, on completion of the reaction, they have to be separated from the products, a process that can be very expensive.

Some large-scale industrial processes incorporating heterogeneous catalysts are listed below:

Process	Reactants, Product/s	Catalyst	Comment
Sulfuric acid synthesis (Contact process)	$\text{SO}_2 + \text{O}_2, \text{SO}_3$	vanadium oxides	Hydration of SO_3 gives H_2SO_4
Ammonia synthesis (Haber–Bosch process)	$\text{N}_2 + \text{H}_2, \text{NH}_3$	iron oxides on alumina(Al_2O_3)	Consumes 1% of world's industrial energy budget
Nitric acid synthesis (Ostwald process)	$\text{NH}_3 + \text{O}_2, \text{HNO}_3$	unsupported Pt-Rh gauze	Direct routes from N_2 are uneconomical
Hydrogen production by Steam reforming	$\text{CH}_4 + \text{H}_2\text{O}, \text{H}_2 + \text{CO}_2$	Nickel or K_2O	Greener routes to H_2 by water splitting actively sought
Ethylene oxide synthesis	$\text{C}_2\text{H}_4 + \text{O}_2, \text{C}_2\text{H}_4\text{O}$	silver on alumina, with many promoters	Poorly applicable to other alkenes
Hydrogen cyanide synthesis (Andrussov oxidation)	$\text{NH}_3 + \text{O}_2 + \text{CH}_4, \text{HCN}$	Pt-Rh	Related ammoxidation process converts hydrocarbons to nitriles
Olefin polymerization Ziegler–Natta polymerization	propylene, polypropylene	TiCl_3 on MgCl_2	Many variations exist, including some homogeneous examples
Desulfurization of petroleum (hydro-desulfurization)	$\text{H}_2 + \text{R}_2\text{S}$ (idealized organosulfur impurity), $\text{RH} + \text{H}_2\text{S}$	Mo-Co on alumina	Produces low-sulfur hydrocarbons, sulfur recovered via the Claus process

