LITTLE FLOWER COLLEGE
DEPARTMENT OF CHEMISTRY

TOPIC : DEACTIVATION OF CATALYST

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Catalysts deactivation

- Catalyst deactivation , the loss overtime of catalytic activity and selectivity ,is a problem of great economic concern in application of commercial catalytic processes .
- Catalyst deactivation is attributed to interaction between the catalyst and the impurities present in process effluent in which the catalyst is used
- Deactivation leads to shortened catalyst lifetime, and the replacement of catalyst is determined by industrial process.
- Industrial catalytic deactivation can range from short term to several years.
- Heterogeneous catalysts are more prone to deactivation

Mechanism	Type	Brief definition/description
Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction.
Fouling, Coking	Mechanical or Chemical	Physical deposition of species (carbonaceous material) from fluid phase onto the catalytic surface and in catalyst pores.
Sintering(Thermal degradation)	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase–support reactions.
Chemical reactions; And Phase transformations	Chemical	Chemical Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase. Reaction of gas with catalyst phase to produce volatile compound.
Attrition/Crushing	Mechanical	Loss of catalytic material due to abrasion, Loss of internal surface area due to mechanical-induced crushing of catalyst

DEACTIVATION MECHANISMS

➢ POISIONING

- Not only blocks the active sites, but also induce changes in the electronic or geometric structure of the surface.

Poisons mainly include

- Groups VA and VIA elements (N, P, As , Sb, O, S , Se, Te)
- Group VIIA elements (F, Cl , Br , I)
- Toxic heavy metals and ions (Pb , Hg , Bi , Sn , Zn , Cd, Cu , Fe)
- Molecules which adsorb with mutiple bonds (CO , NO, HCN , benzene)

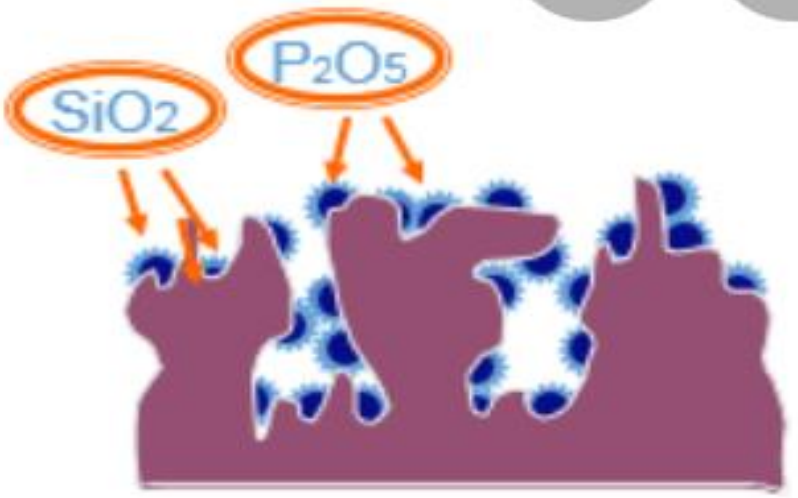
A substance which destroys the activity of the catalyst to accelerate a reaction, is called a poison and the process is called Catalytic Poisoning.

Example: -

$$2SO_2 + O_2 + [Pt] \longrightarrow 2SO_3$$

This is poisoned by As_2O_3

Non-Poisoned Catalyst Surface



Poisoned Catalyst Surface

- Poisoning is the strong chemisorption of reactants , products or impurities on sites otherwise available for catalysis.
- Whether a species act as a poison depends upon its adsorption strength relative to other species competing for catalytic sites.
- Poisoning may be reversible or irreversible .
- Poisoning whether reversible or irreversible , deactivation effect while poison is absorbed on surface is same.
- Many poisons occur naturally in feed stream that is treated in catalytic processes. Eg ; crude oil contains sulfur and metals , such as vanadium and nickel , act as poison for many refinery processes.

•Some poisons may be added purposefully , either to moderate the activity or to alter the selectivity of fresh catalysts or to improve the performance of the product that is later reprocessed.

MECHANISMS BY WHICH A POISON AFFECT CATALYTIC ACTIVITY

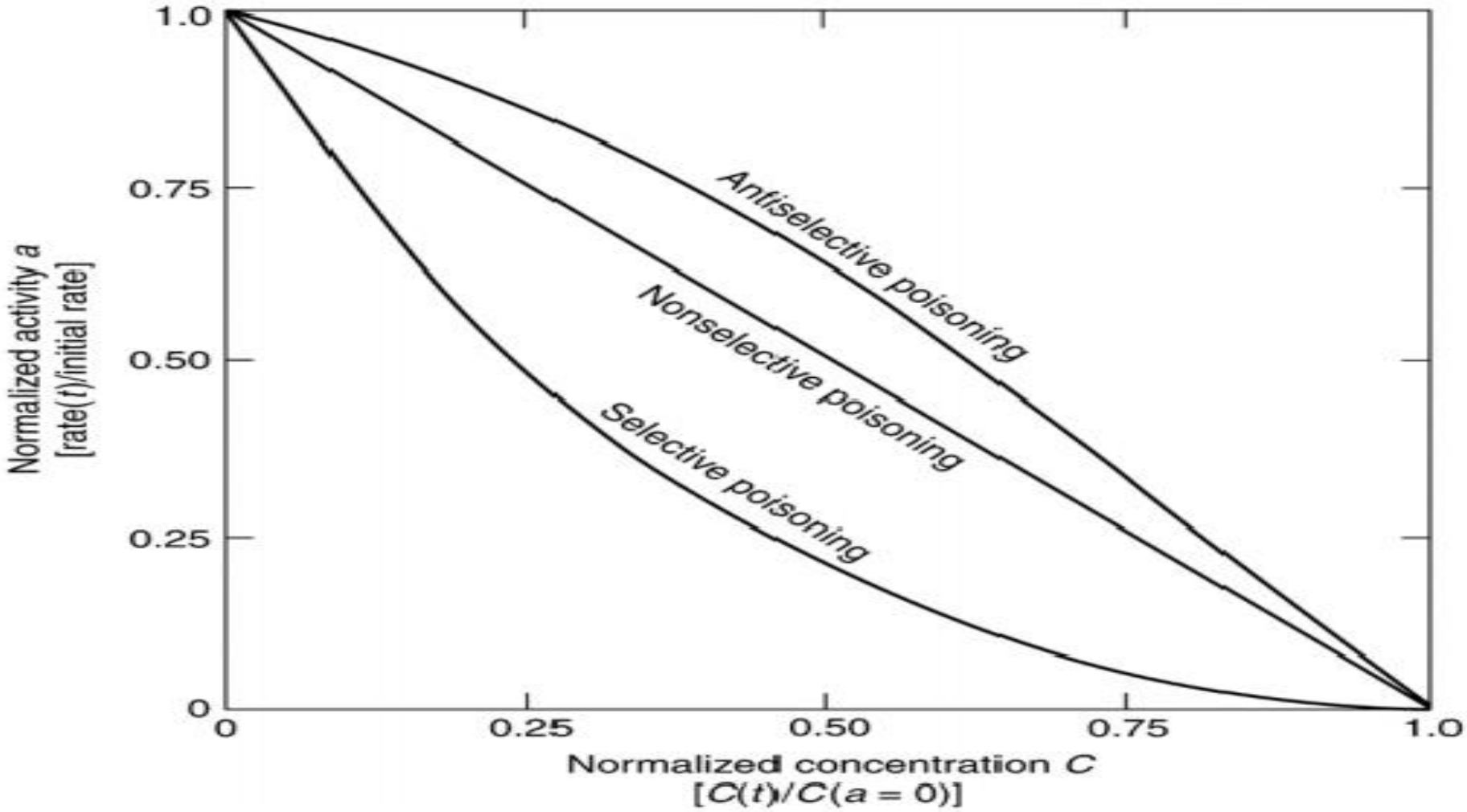
- A strongly adsorbed atom of sulfur physically blocks at least one adsorption or reaction site .
- By virtue of its strong chemical bond , it electronically modifies its neighbour atom , thereby modifying their ability to adsorb reactant molecules

- Third effect is restructuring of surface by strongly adsorbed poison ,causing changes in catalytic properties .

- Adsorbed poison blocks access of adsorbed reactants to each other .
- It prevents or slows the surface diffusion of adsorbed reactants.

Poisoning selectivity

A plot of activity versus normalised poison concentration



Types:

- Selective – involves preferential adsorption of the poison on the most active sites at low concentration
- Reversible
- Anti – selective – sites of lesser activity are blocked initially , such poisoning is called anti selective
- Non – reversible
- Non- selective- if the activity loss is proportional to the concentration of adsorbed poison , the poisoning is non – selective .

Industrial examples of catalyst deactivation due to poisoning

Reaction	Catalyst	Poisons
Catalytic Cracking	Silica-alumina, Zeolites	Organic bases, hydrocarbons heavy metals
Hydrogenation , dehydrogenation	Nickel, Platinum, Palladium	Compounds of S, P, As, Zn, Hg, halides, Pb, NH_3, C_2H_2
Steam reforming of methane, naphtha	Nickel	H_2S, As
Ammonia synthesis	Iron or Ruthenium	O_2, H_2O, CO, S, C_2H_2, H_2O
Fischer–Tropsch synthesis	Cobalt or Iron	H_2S, COS, As, NH_3, metal carbonyls
Hydrocracking	Noble metals on zeolites	NH_3, S, Se, Te, P

OXYGEN POISONING

- Oxygenated molecules present in feedstock.

NITROGEN POISONING

- Impurities in feed like alkyl derivatives of pyridine , quinoline , isoquinoline , phenanthrilidine.
- Prevented by hydrotreatment , adsoption , liquid extraction.

SULPHUR POISONING

- non hydrotreated feeds like alkylated thiophenes , benzothiophenes and dibenzothiophenes .
- sulphur contained coke on oxidation in regenerator produce toxic SOx

Basic mechanism	problems		Method of minimization
			•Purity feed or use guard bed to adsorb poison •Employ additives
poisoning	Loss of catalytic surface sites		•Choose reaction condition that lower adsorption strength
			•Optimize pore structure •Apply coating that serves as diffusion barrier to poison

THANK YOU