

WHAT IS CATALYSIS

- Catalysis is the chemical reaction brought about by a **catalyst**.
- Catalyst is a material that **increases the rate of a chemical reaction** while itself **not** undergoing any permanent **change**.
- The term “**catalysis**” was introduced as early as 1836 by **Berzelius**.
- **There are two classes**
 1. ***Positive catalyst*** - increase the rate of the reaction.
 2. ***Negative catalyst***- decrease the rate of the reaction.

According to berzelius

- The name 'catalysis' was coined by Berzelius in 1836.
- He concluded that besides 'affinity' a new force is operative, the 'Catalytic Force'.
- With this, try to focus the behavior of some substances that permit initiate reaction of decomposition or synthesis.
- At that time no understanding existed, on a molecular level, of reaction rates.

- For a chemical reaction to take place, it requires a certain minimum amount of energy, called its **activation energy E_a** .
- If a **substance** can lower this activation energy without itself being changed or consumed during the reaction, it is called a **catalyst** or **catalytic agent**. The action of a catalyst is called *catalysis*.
- The catalyst reduces the activation energy by providing an alternative pathway for the reaction to occur.

Three key aspects of catalyst action

- ❖ **Taking Part In The Reaction** it will change itself during the process by interacting with other reactant/product molecules.
- ❖ **Altering The Rates Of Reactions** In most cases the rates of reactions are increased by the action of catalysts; however, in some situations the rates of undesired reactions are selectively suppressed
- ❖ **Returning to its original form** After reaction cycles a catalyst with exactly the same nature is 'reborn.

In practice a catalyst has its lifespan - it deactivates gradually during use

GENERAL REQUIREMENTS FOR A GOOD CATALYST

- *Catalytic Activity*
- *Catalytic Selectivity.*
- *Catalytic Stability*

Catalytic Activity

- A catalyst should be able to pass through the catalytic cycle multiple times. Higher the number of times the catalyst passes through this cycle, higher is the activity of the catalyst.
- The number of times that a catalyst can go through this cycle converting substrate molecule to product molecules is defined as the **turnover number**.
- In homogeneous systems, **the turnover frequency** is defined as the number of molecules of substrate converted per second which is the turnover number in a certain period of time.

- It depends upon adsorption of reactants on the surface of catalyst.
- Chemisorption is the main factor governing the activity of catalysts.
- The bond formed during adsorption between the catalytic surface and the reactants must not be too strong or too weak.

Catalytic Selectivity

- Catalysts are highly specific compounds.
- They have an ability to direct the reaction to yield a particular product.
- The reaction with same reactants but different catalyst may yield different products.
- This is termed as the selectivity of catalyst. Catalysts are highly selective in nature.

Catalytic Stability

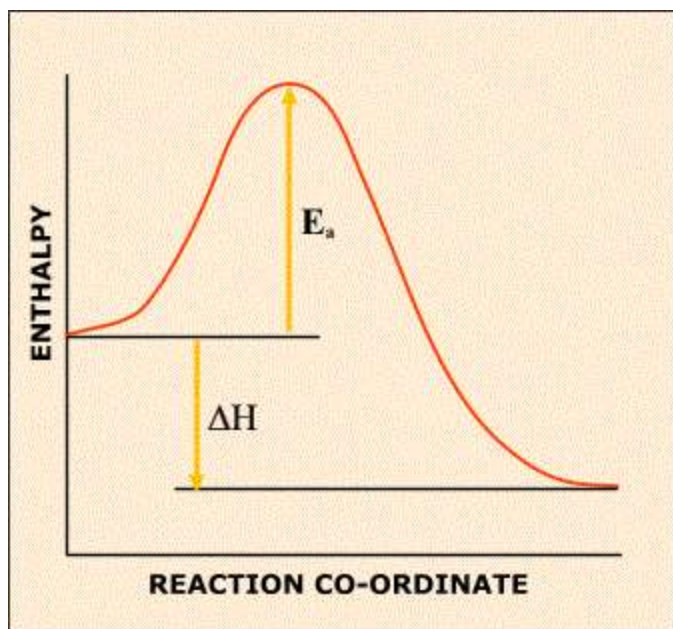
A **good catalyst** should **resist to deactivation**, caused by

- The presence of impurities in feed (e.G. Lead in petrol poison TWC.
- Thermal deterioration, volatility and hydrolysis of active components
- Attrition due to mechanical movement or pressure shock

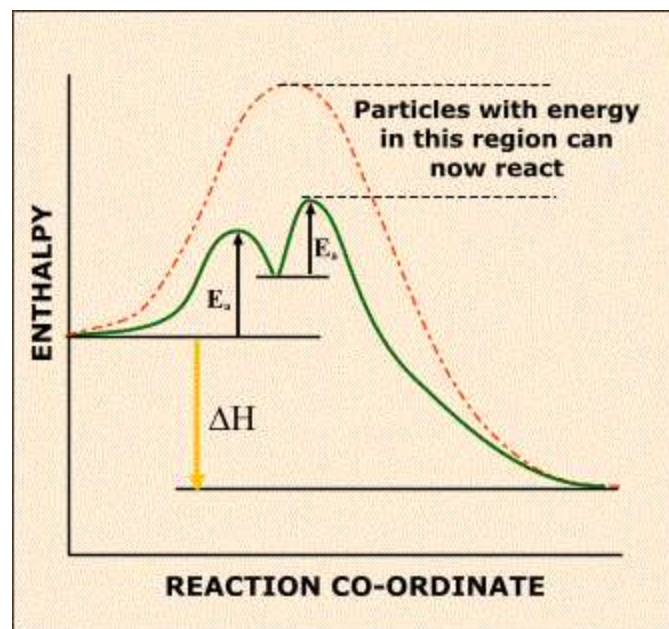
A solid catalyst should have reasonably large surface area needed for reaction (active sites). This is usually achieved by making the solid into a porous structure

CATALYSTS - lower E_a

Catalysts work by providing... **“an alternative reaction pathway which has a lower activation energy”**



With out catalyst



with catalyst

A GREATER PROPORTION OF PARTICLES WILL HAVE ENERGIES IN EXCESS OF THE MINIMUM REQUIRED SO MORE WILL REACT

TYPES OF CATALYSTS & CATALYTIC REACTIONS

- **The types of catalysts**
 - *Classification based on the its physical state, a catalyst can be*
 - gas
 - liquid
 - solid
 - *Classification based on the substances from which a catalyst is made*
 - Inorganic (gases, metals, metal oxides, inorganic acids, bases etc.)
 - Organic (organic acids, enzymes etc.)

– *Classification based on the ways catalysts work*

- Homogeneous - both catalyst and all reactants/products are in the same phase (gas or liq)
- Heterogeneous - reaction system involves multi-phase (catalysts + reactants/products)

– *Classification based on the catalysts' action*

- Acid-base catalysts
- Enzymatic
- Photocatalysis
- Electrocatalysis, etc.

EXAMPLES OF CATALYSTS

Metals

Ni, Pt

hydrogenation reactions

Fe

Haber Process

Rh, Pd

catalytic converters

Oxides

Al_2O_3

dehydration reactions

V_2O_5

Contact Process

FINELY DIVIDED

increases the surface area

provides more collision sites

IN A SUPPORT MEDIUM maximises surface area and reduces costs

Catalytic processes can be divided in three main types:

- Heterogeneous reaction
- Homogeneous reaction
- Enzymatic catalysis (biocatalysis)

Heterogeneous Catalysis

- Catalysts are in a **different phase** to the reactants **usually solid state** e.g. a solid catalyst in a gaseous reaction.
- It is characterized by the presence of “active sites” on the catalyst surface.

Action takes place at **active sites** on the surface of a solid
gases are adsorbed onto the surface they form weak bonds
with metal atoms.

e.g. decomposition of H_2O_2 with MnO_2 as catalyst

Solid Catalysts

– Active phase

- Where the reaction occurs (mostly metal/metal oxide)

– Promoter

- Textual promoter (e.g. Al - Fe for NH_3 production)
- Electric or Structural modifier
- Poison resistant promoters

– Support / carrier

- Increase mechanical strength
- Increase surface area (98% surface area is supplied within the porous structure)
- may or may not be catalytically active

Solid Catalysts

- Some common solid support / carrier materials
 - Alumina
 - Inexpensive
 - Surface area: 1 ~ 700 m²/g
 - Acidic
 - Silica
 - Inexpensive
 - Surface area: 100 ~ 800 m²/g
 - Acidic
 - Zeolite
 - mixture of alumina and silica,
 - often exchanged metal ion present
 - shape selective

Solid Catalysts

Other supports

- Active carbon (S.A. up to 1000 m²/g)
- Titania (S.A. 10 ~ 50 m²/g)
- Zirconia (S.A. 10 ~ 100 m²/g)
- Magnesia (S.A. 10 m²/g)
- Lanthana (S.A. 10 m²/g)

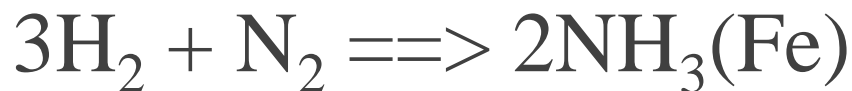
Homogeneous Catalysis

- Catalyst and reactants are in the **same phase usually in aqueous state**
- Reaction proceeds through an intermediate species with lower energy
- There is usually more than one reaction step
- Transition metal ions are often involved - oxidation state changes.

Several homogeneous catalytic systems are

1. Acid base catalysis
2. Catalysis by metal ions
3. Catalysis by organometallic complexes
4. Catalysis by Lewis acids
5. Catalysis by porphyrin complexes
6. Catalysis by enzymes

- ***Haber Process***



- ***Contact Process***



- ***Hydrogenation of C=C***

(hardening of oil - vegetable oil to margarine)



Catalysts Characterization

Characteristics	Methods
Surface area, pore volume & size	N ₂ Adsorption-Desorption Surface area analyzer (BET and Langmuir)
Pore size distribution	BJH (Barret, Joyner and Halenda)
Elemental composition of catalysts	Metal Trace Analyzer / Atomic Absorption Spectroscopy
Phases present & Crystallinity	X-ray Powder Diffraction TG-DTA (for precursors)
Morphology	Scanning Electron Microscopy

Catalyst reducibility	Temperature Programmed Reduction
Dispersion, SA and particle size of active metal	CO Chemisorption, TEM
Acidic/Basic site strength	NH ₃ -TPD, CO ₂ TPD
Surface & Bulk Composition	XPS
Coke measurement	Thermo Gravimetric Analysis, TPO

Applications of Catalysis

Industrial applications

Almost all chemical industries have one or more steps employing catalysts

1. Petroleum, energy sector, fertiliser, pharmaceutical, fine chemicals

Environmental applications

– **Pollution controls in combination with industrial processes**

- ❖ Pre-treatment - reduce the amount waste/change the composition of emissions
- ❖ Post-treatments - once formed, reduce and convert emissions
- ❖ Using alternative materials

– **Pollution reduction**

- ❖ gas - converting harmful gases to non-harmful ones
- ❖ liquid - de-pollution, de-odder, de-colour etc
- ❖ solid - landfill, factory wastes

Advantages of catalytic processes

- **Achieving better process economics and productivity**
 - ❖ Increase reaction rates - fast
 - ❖ Simplify the reaction steps - low investment cost
 - ❖ Carry out reaction under mild conditions (e.g. low T, P)
 - low energy consumption
- **Reducing wastes**
 - ❖ Improving selectivity toward desired products - less raw materials required, less unwanted wastes
 - ❖ Replacing harmful/toxic materials with readily available ones

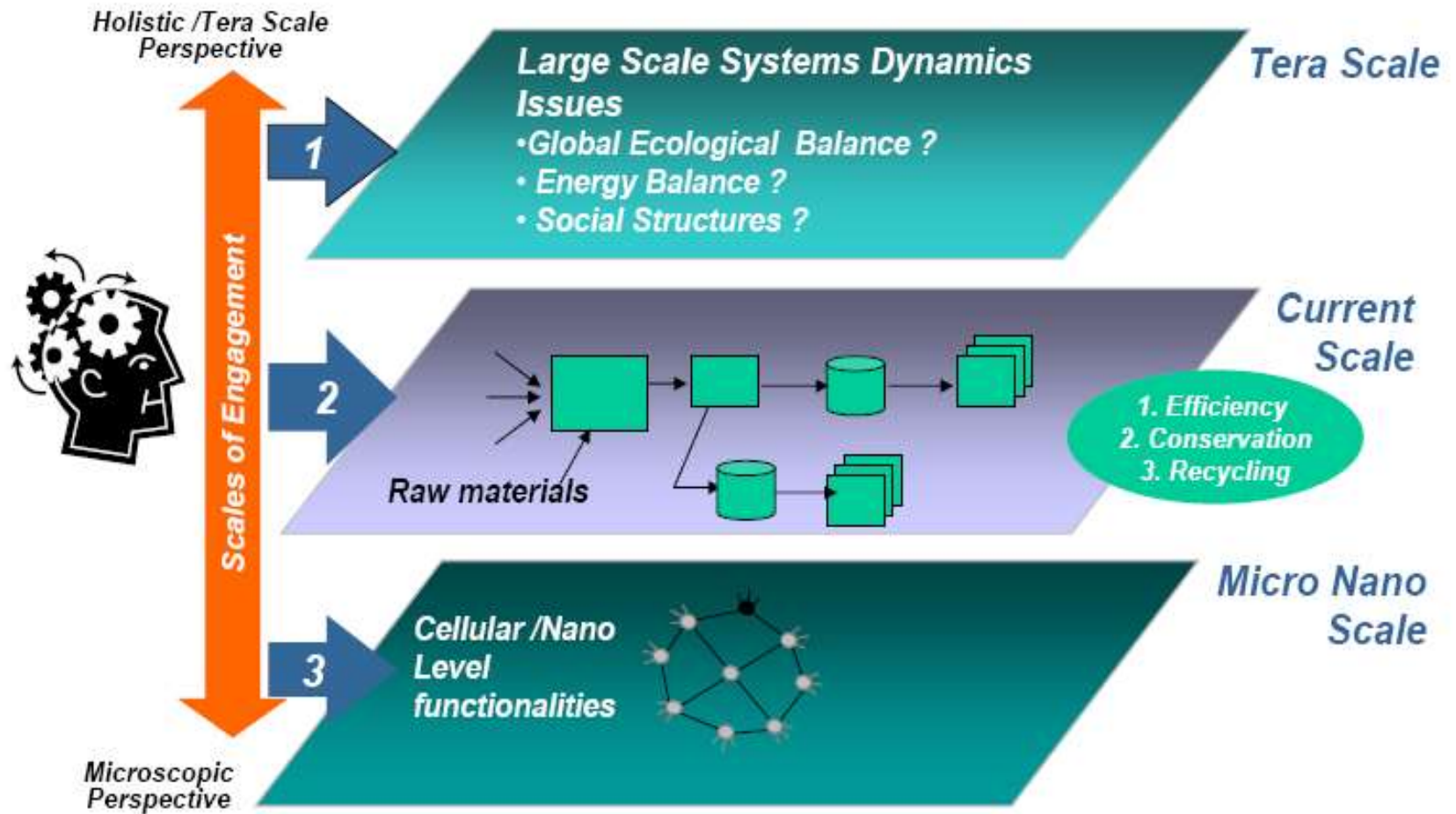
- Producing certain products that may not be possible without catalysts
- Having better control of process (safety, flexible etc.)
- Encouraging application and advancement of new technologies and materials

History of catalyst

- "Catalyst", a term derived from greek meaning "to annul," or "to untie," or "to pick up."
- The concept of catalysis was invented by chemist [elizabeth fulhame](#) and described in a 1794 book, based on her novel work in oxidation-reduction experiments.
- The term *catalysis* was later used by [jöns jakob berzelius](#) in 1835 to describe reactions that are accelerated by substances that remain unchanged after the reaction

History of catalyst

- **Three Scales of Knowledge Application**

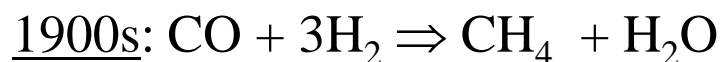


Some Developments in Industrial catalysis-1

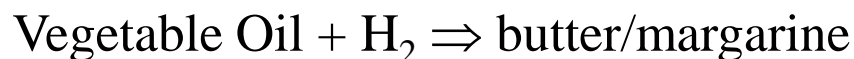
1900- 1920s

Industrial Process

Catalyst



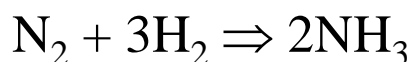
Ni



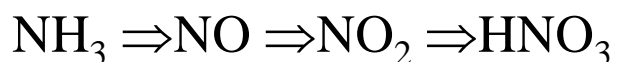
Ni



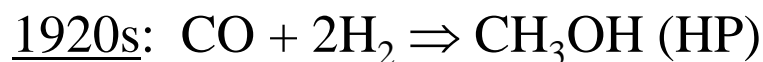
Ni



Fe/K



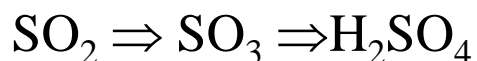
Pt



(ZnCr)oxide



Co,Fe

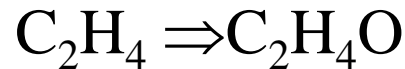


V_2O_5

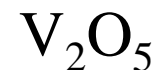
Industrial catalysis-2 (1930s and 1940s)

1930s:Cat Cracking(fixed,Houdry)

Mont.Clay



Ag



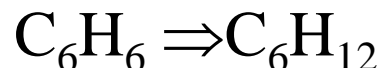
1940s:Cat Cracking(fluid)

amorph. SiAl

alkylation (gasoline)

HF/acid- clay

Platforming(gasoline)



Ni

Industrial catalysis-3 (1950s)

$\text{C}_2\text{H}_4 \Rightarrow \text{Polyethylene(Z-N)}$	Ti
$\text{C}_2\text{H}_4 \Rightarrow \text{Polyethylene(Phillips)}$	Cr-SiO ₂
Polyprop & Polybutadiene(Z-N)	Ti
Steam reforming	Ni-K- Al ₂ O ₃
HDS, HDT of naphtha	(Co-Mo)/Al ₂ O ₃
$\text{C}_{10}\text{H}_8 \Rightarrow \text{Phthalic anhydride}$	(V,Mo)oxide
$\text{C}_6\text{H}_6 \Rightarrow \text{C}_6\text{H}_{12}$	(Ni)
$\text{C}_6\text{H}_{11}\text{OH} \Rightarrow \text{C}_6\text{H}_{10}\text{O}$	(Cu)
$\text{C}_7\text{H}_8 + \text{H}_2 \Rightarrow \text{C}_6\text{H}_6 + \text{CH}_4$	(Ni-SiAl)

Industrial catalysis-4 (1960s)

Butene \Rightarrow Maleic anhydride	(V,P) oxides
$C_3H_6 \Rightarrow$ acrylonitrile(ammox)	(BiMo)oxides
Bimetallic reforming	PtRe/ Al_2O_3
Metathesis($2C_3 \Rightarrow C_2 + C_4$)	(W,Mo,Re)oxides
Catalytic cracking	Zeolites
$C_2H_4 \Rightarrow$ vinyl acetate	Pd/Cu
$C_2H_4 \Rightarrow$ vinyl chloride	$CuCl_2$
O-Xylene \Rightarrow Phthalic anhydride	V_2O_5/TiO_2

Industrial catalysis-5

1970s

Xylene Isom(for p-xylene)	H-ZSM-5
Methanol (low press)	Cu-Zn/Al ₂ O ₃
Toluene to benzene and xylenes	H-ZSM-5
Catalytic dewaxing	H-ZSM-5
Autoexhaust catalyst	Pt-Pd-Rh on oxide
Hydroisomerisation	Pt-zeolite
SCR of NO(NH ₃)	V/ Ti
MTBE	acidic ion exchange resin
$C_7H_8 + C_9H_{12} \Rightarrow C_6H_6 + C_8H_{10}$	Pt-Mordenite

Industrial catalysis-6 (1980s)

Ethyl benzene	H-ZSM-5
Methanol to gasoline	H-ZSM-5
Vinyl acetate	Pd
Improved Coal liq	NiCo sulfides
Syngas to diesel	Co
HDW of kerosene/diesel.GO/VGO	Pt/Zeolite
MTBE cat dist	ion exchange resin
Oxdn of methacrolein	Mo-V-P
N-C6 to benzene	Pt-zeolite

Industrial catalysis-7(1990^s)

DMC from acetone	Cu chloride
NH ₃ synthesis	Ru/C
Phenol to HQ and catechol	TS-1
Ammoximation of cyclohexanone	TS-1
Isom of oxime to caprolactam	TS-1
Ultra deep HDS	Co-Mo-Al
Olefin polym	Supp. metallocene cats
Ethane to acetic acid	Multi component oxide
Fuel cell catalysts	Rh, Pt, ceria-zirconia

Industrial catalysis-8

2000+

- Solid catalysts for biodiesel
 - solid acids, Hydroisom catalysts
- Catalysts for carbon nanotubes
 - Fe (Ni)-Mo-SiO₂

Why are Catalysts Important?

Catalysts can:

- Make a reaction possible under achievable conditions.
- **Reduce** the necessity of expensive & dangerous conditions.
- Generate **high yields** and **high product purity**.
- Reduce the amount of side-product and waste created
generate non-racemic mixtures of enantiomers.
- Make a chemical process “**greener**”.



Thank you