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# Catalyst and Catalysis

Catalyst  $\Rightarrow$  Catalyst is a substance which quickens or retards the rate of chemical reaction by altering the path of a reaction. Or, A catalyst is the chemical substance that lowers the activation energy barrier by creating a new route to the given chemical reaction and such process is called Catalysis.

## Types of Catalysis.

Catalysis can be of various types, with the primary classification dividing them into homogenous catalysis and heterogenous catalysis on the basis of phase compared to the reactant.

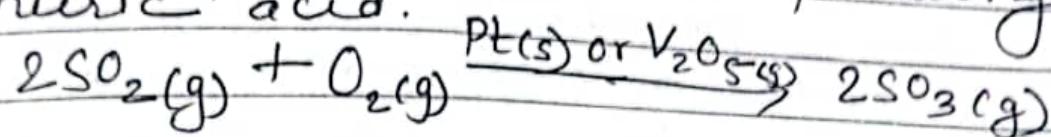
### 1. Heterogenous Catalysis :-

The catalytic process in which the catalyst material is in different phase from that of reactant. The majority of heterogenous catalysis consists of solid catalyst with liquid or gas phase reactants. It is also called contact catalysis since the reaction occurs by contact of reactants with the

catalyst surface. This form of catalysis has great industrial importance.

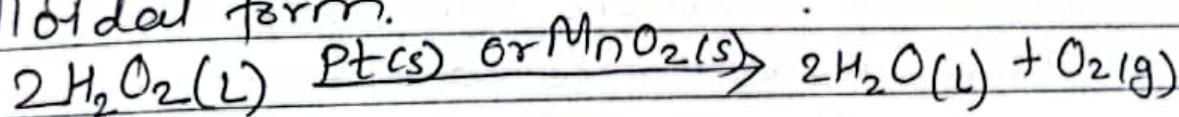
Example:-

i) Heterogeneous Catalysis with gaseous reactants (contact catalysis): Combination of Sulphur dioxide and oxygen in the presence of finely divided platinum or vanadium pentoxide to give  $\text{SO}_3$  in contact process for manufacturing sulphuric acid.



ii) Heterogenous catalysis with liquid reactants:-

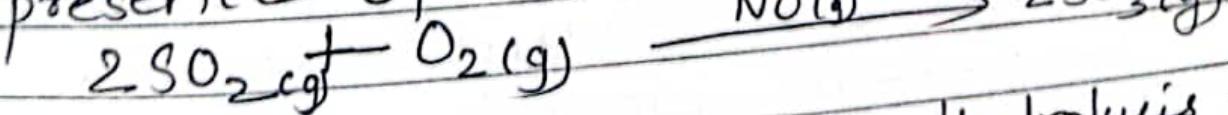
The decomposition of aqueous solution of hydrogen peroxide is catalysed by manganese dioxide or platinum in colloidal form.



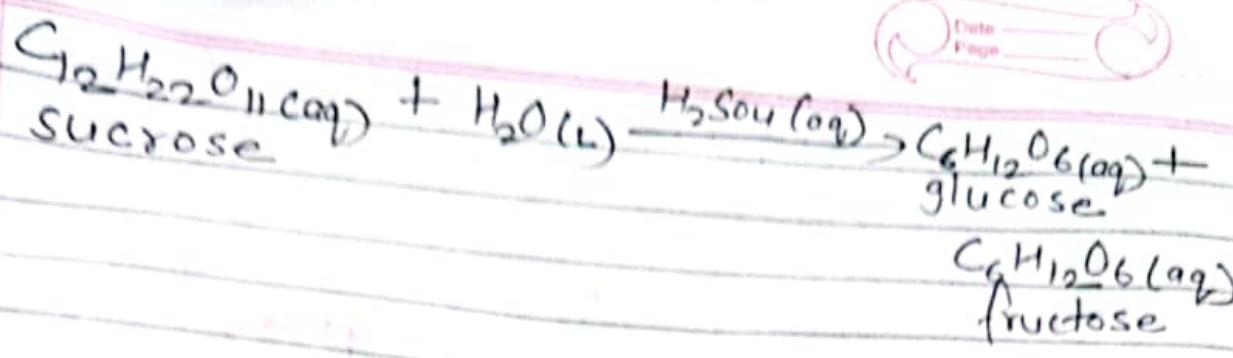
2. Homogenous Catalysis:- The catalytic process in which the catalyst material are in the same phase to that of reactant

Example:-

i) Catalysis in gas phase:- Oxidation of Sulphur dioxide to sulphur trioxide in presence of nitric oxide as catalyst.



ii) Catalysis in solution phase:- Hydrolysis of sucrose in aqueous solution in the presence of mineral acid as catalyst.



## Structure-activity Relationship:

In catalysis, specific surface area, pore size, and pore volume of catalyst play a pivotal role in shaping the properties and effectiveness of catalyst.

The specific surface area of a catalyst influences the reaction rate in heterogeneous catalysis. The enhanced surface area helps to reduce mass transfer limitation between the two phases involved in the chemical reaction. High specific surface area can enhance dispersion, leading to smaller catalyst particle size and greater number of active site, but this alone is insufficient. Highly porous structure are responsible for proper ionic mobility.

Microporous substance such as Zeolites, silicas, activated Carbon have been extensively utilized as catalyst and catalyst support.

The pores are classified in different types depending on their size.

a) micro pore (size  $< 2\text{ nm}$ )

b) meso pore ( $2\text{ nm} < \text{Size} < 50\text{ nm}$ )

c) macropore ( $\text{Size} > 50\text{ nm}$ )

④ chemical reactions catalyzed over mesoporous catalyst:

Reaction  
Friedel-Craft alkylation

Mesoporous catalyst  
Aluminium Iso Propoxide

Adol condensation

Al - substituted.

Reckmann rearrange-  
ment

Al - substituted

Crucial characteristics of these porous nanomaterials involves their crystallinity and the extent of long range order. These factors notably govern their activity and selectivity but also impact their mechanical properties which are crucial for their processability.

Achieving the right formulation of the catalyst involves finding a balance between effective fluid flow, activity and stability. In figure 38 below, elements are depicted as the three parts of the circle, underscoring their interdependence and mutual interaction.

The catalyst with proper shape and size with good mechanical strength can maintain effective fluid flow distribution and minimal pressure drop required for effective catalysis

e.g. hydrotreating catalyst (used in petroleum refineries),  $\text{CoMo}/\text{Al}_2\text{O}_3$  com-

in various shapes and sizes like pellets, extrudates and spheres ranging from 1 to 10mm whether the feedstock is light naphtha gas oil or vacuum residue. The porosity and high surface area lead to the enhancement of catalytic activity. The selection of appropriate material and preoperational method to achieve high activity specific surface area and porous structure is crucial task for the formulation of catalyst with high activity and selectivity. Achieving activity alone is not sufficient, it must be balanced with consideration for lifetime stability i.e., resistance to deactivation from sintering, poisoning and fouling.

The factors such as optimal activity, lifetime, selectivity, compatibility etc must be taken under consideration while designing and development of catalyst.

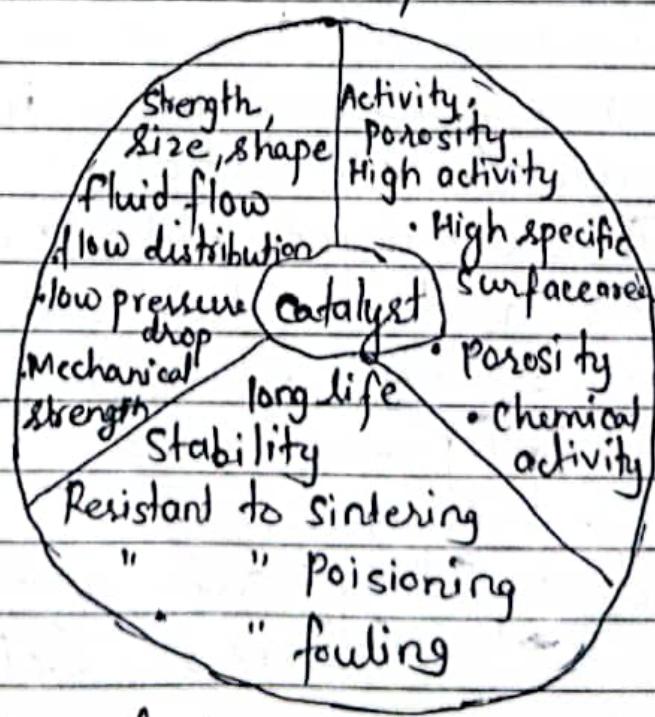


fig: Engineering features of a catalyst

# Catalysis for Energy and Environmental Applications

## Catalytic Conversion of fossil fuels

The most viable and economical technology for the production of hydrogen is catalytic conversion of fossil fuels.

The commonly employed methods for the catalytic conversion of fossil fuel to hydrogen are pyrolysis, partial oxidation, autothermal and steam reforming. The Ni /  $\text{Al}_2\text{O}_3$  catalyst is considered as the most cost-effective and efficient catalyst which remarkably suppress the coke formation.

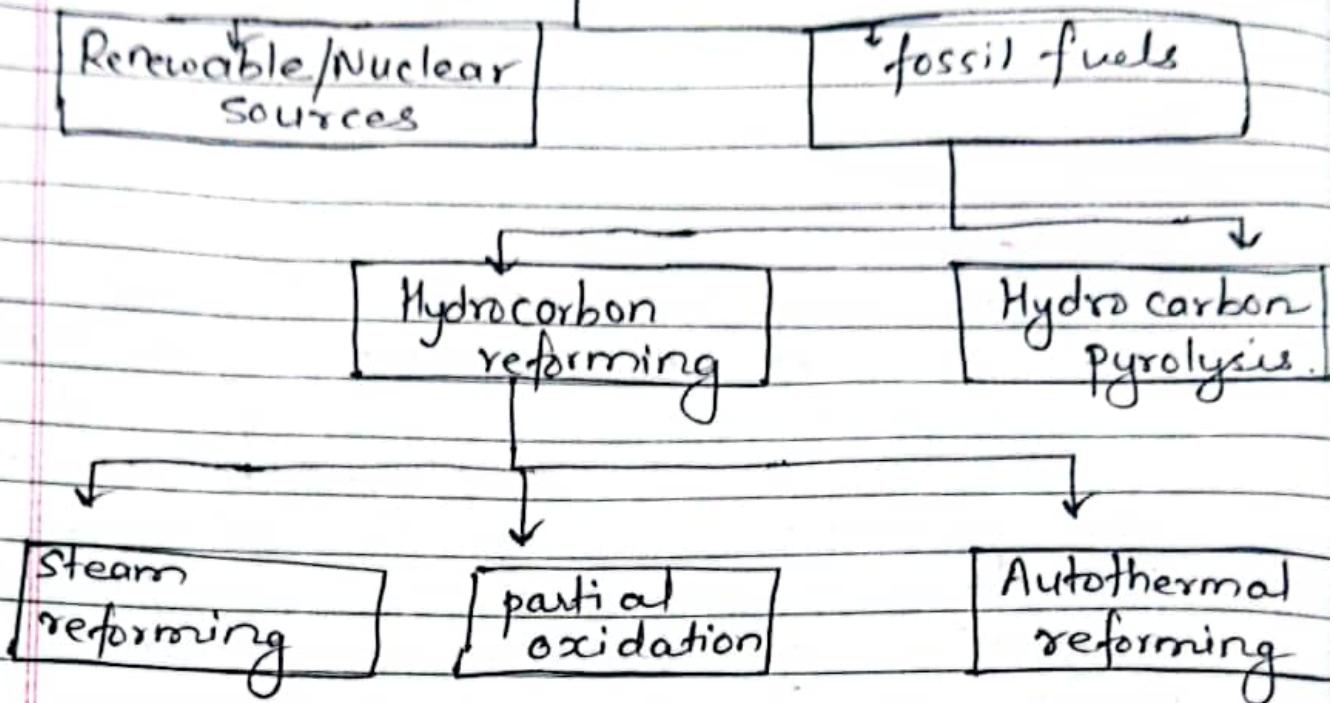
Hydrogen produced by water electrolysis or photolysis technologies is called as green hydrogen. Similarly, the hydrogen commonly produced through reform process using hydrocarbon fuel is called as gray hydrogen.

Oil reforming stands out as a significant commercial technology for the production of hydrogen. Light oils having relative low molecular weight are more advantageous in hydrogen production compared to heavy oils like bitumen or residual oil.

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## Hydrogen Production



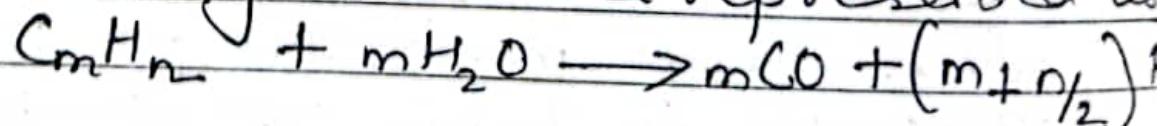
Generally four reforming techniques are employed for hydrogen production from fossil fuels. These technique also utilize methane as a raw material.

### (a) Steam Reforming:

The primary objective of this process is to produce safe, economical and sustainable hydrogen economy.

Steam reforming is commonly preferred process for the production of hydrogen from natural gas and oil.

Chemically it can be represented as



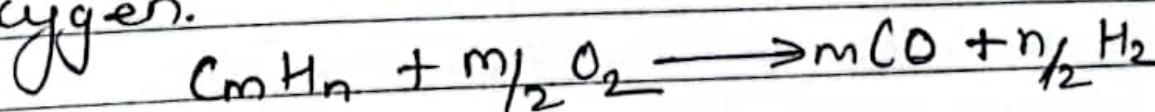
It is an endothermic reaction which demands an external heat source.

(8) It offers several advantages such as a need of oxygen, a lower operating temperature compared to partial oxidation (POX) and autothermal reforming with high H<sub>2</sub> to CO ratio (3:1). The high ratio of H<sub>2</sub> to CO is advantageous for hydrogen production.

### b) Partial oxidation (POX):-

The partial oxidation (POX) of hydrocarbon and catalytic partial oxidation (CPOX) of oil have been suggested for hydrogen production in fuel cells for automobiles and various commercial applications.

This process involves converting oil into hydrogen by partially oxidising (combusting) the hydrocarbon with oxygen.



Partial oxidation offers advantages such as minimal methane slip, increased sulfur tolerance and a favourable H<sub>2</sub> to CO ratio. However, the non-catalytic partial oxidation process requires operation at high temp (1300 - 1500 °C) to mitigate coke formation.

This process needs an expensive and complicated oxygen separation unit to provide pure oxygen to the reactor.

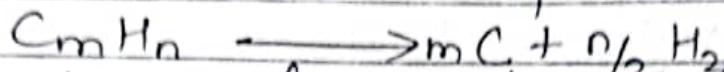
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### c. Pyrolysis:

Pyrolysis is the another technology for the production of hydrogen which involves the thermal decomposition of raw oil into hydrogen and Carbon.

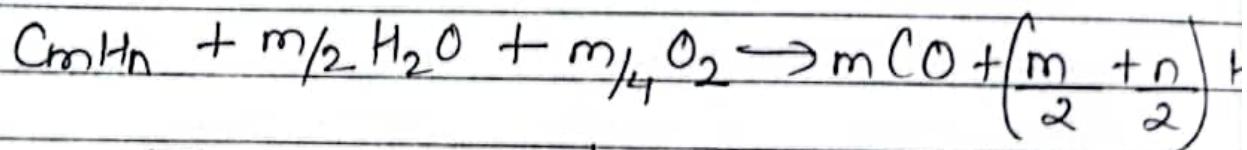
The reaction can be expressed as;



There is no possibility of formation of CO or CO<sub>2</sub> as no water is used nor the air. Advantage of this approach include fuel flexibility, relative simplicity and compactness, a clean carbon by product and a decrease in CO<sub>2</sub> and CO emissions. There may be potential for fouling of catalyst due to Carbon formed during the reaction but appropriate design can minimize this issue.

### d. Autothermal reforming (ATR):

It involves adding steam to catalytic partial oxidation (CPOX). The chemical change of ATR can be expressed as follows:-



It is carried out as lower pressure compare to partial oxidation (POX) reforming and exhibit low methane slip. It comprises a thermal zone where either POX or CPOX is utilized to generate the heat required to drive

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down-stream steam-reforming reaction in a catalytic zone. A notable advantage of this process over steam-reforming is its ability to be rapidly started and stopped while producing a greater quantity of hydrogen than POX alone.

For ATR to function effectively, the oxygen-to-fuel ratio and the steam-to-carbon ratio must be controlled at all times to regulate reaction temperature, product gas composition and prevent coke formation. Similar to POX, this process also requires an expensive oxygen separation unit.

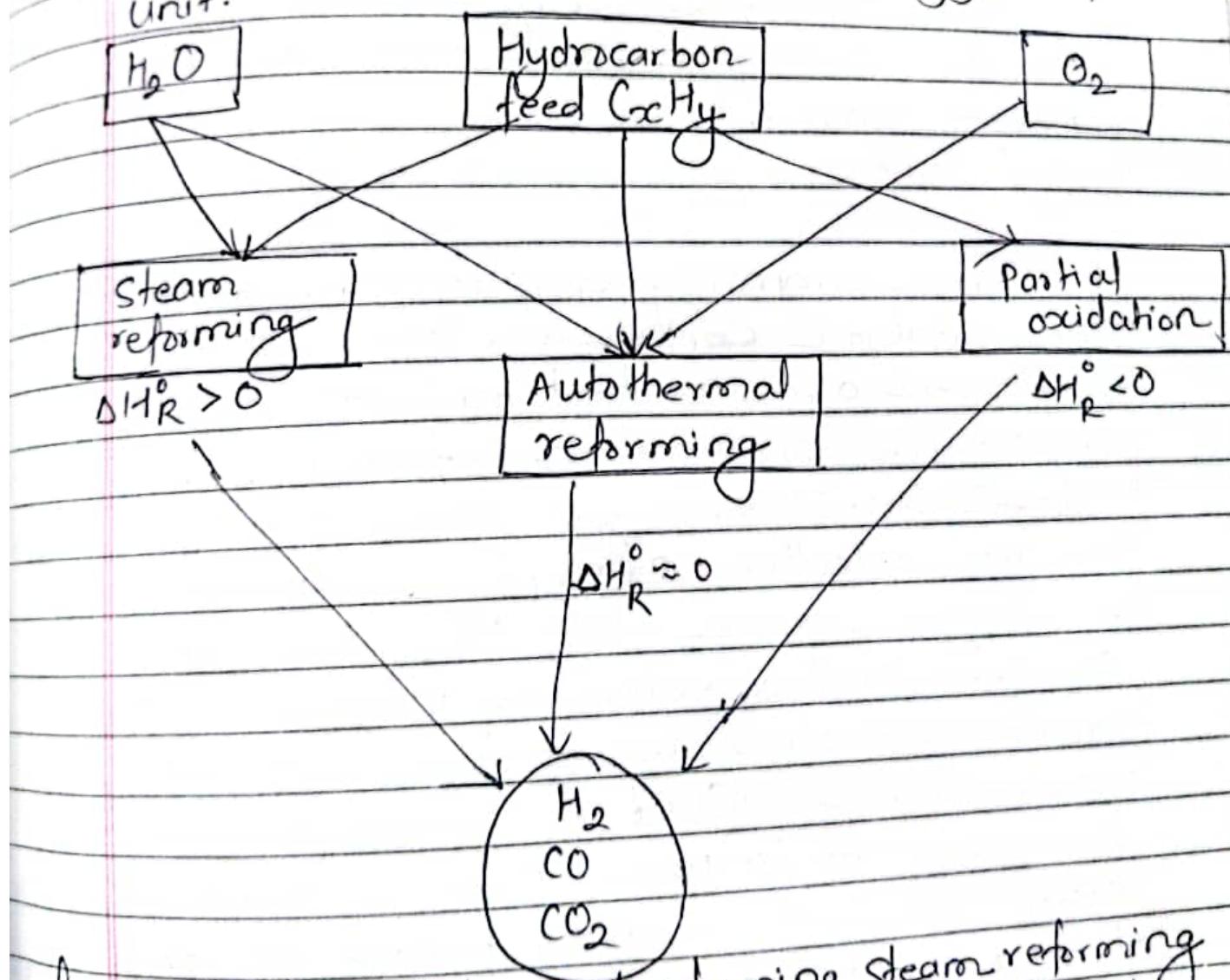


fig: Pyrolysis, autothermal reforming, steam reforming, partial oxidation of hydrocarbons.

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## Catalyst for Pollution Control.

Catalyst are used for the reduction of air pollutant gases from the atmosphere and toxic organic pollutants present in water body. They convert  $\text{CO}_2$  gas into alcohol and reduce the  $\text{CO}_2$  concentration in atmosphere. They degrade toxic organic molecules present in water as well as in air (VOCs) into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

### ⓐ Catalytic reduction of greenhouse gas emissions.

Two specific scenarios are examined for the catalytic reduction of green house gases.

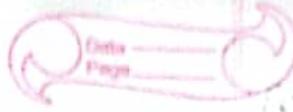
#### ⓐ Reduction of anthropogenic emissions of non $\text{CO}_2$ , GHGs ( $\text{N}_2\text{O}$ and $\text{CH}_4$ )

The commonly employed methods for the catalytic conversion of methane to hydrogen are partial oxidation, dry reforming and steam reforming.

$\text{Fe-ZnAl-5}$  catalyst show good performance in the selective catalytic reduction (SCR) of nitrogen oxides ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ) with oxygen and a selective inorganic or organic reducing agent. The catalytic conversion of CFCs to fluorocarbon is best way to improve ozone layer depletion. Metal catalyzed such as palladium on alumina or carbon, aluminium fluoride ( $\text{AlF}_3$ )

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and various oxides exhibit activity in the process of hydrochlorination, converting chlorofluorocarbons (CFCs) into hydrofluorocarbons (HFCs).



### b) Reduction or Conversion of $\text{CO}_2$

$\text{CO}_2$  is the major cause of global warming and is responsible for climate change. Recent attention has centered on catalytic conversion of carbon dioxide into fuels (eg methanol) and other products.

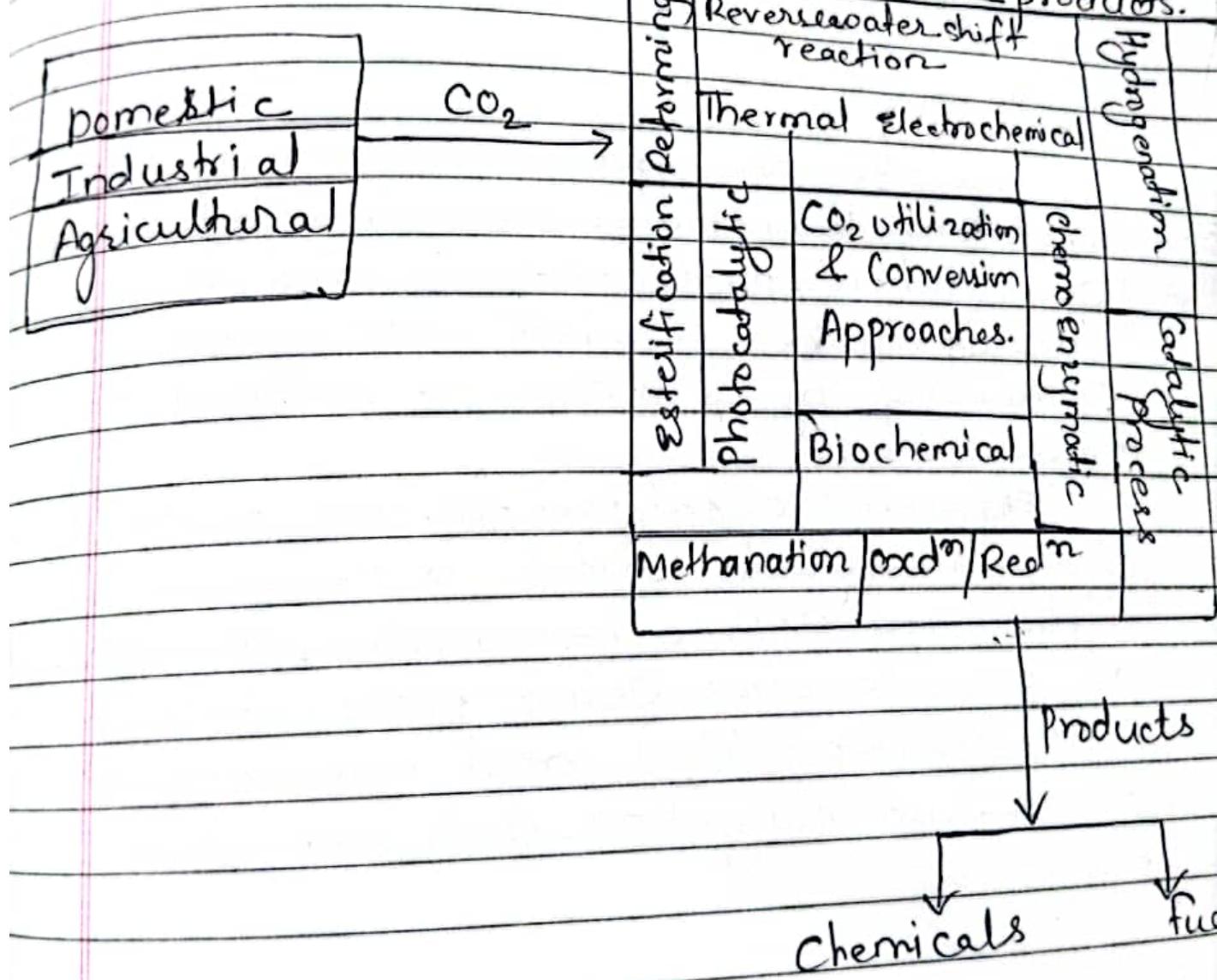


fig: Overview of  $\text{CO}_2$  utilization and conversion approaches.

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list of catalyst used for the production of valuable products through  $\text{CO}_2$  utilization and conversion approaches.

s.N	Catalyst	Products	Approaches.
1.	Nitrogenase	Methane	Chemo- Enzymatic
2.	Pd/H <sub>2</sub> SM-S	Dimethyl ether	Hydrogenation
3.	Zeolite membrane	Methanol	Hydrogenation
4.	RuCl <sub>3</sub> · xH <sub>2</sub> O	formate	Hydrogenation
5.	Nickel (Ni)	Methane	Thermal (reforming)
6.	Indium	Acetate & Formate	Electrochemical.

### Catalytic dye degradation

Despite the implementation of various treatment technologies, including adsorption, coagulation, photocatalysis and biodegradation, the challenges persists with waste water containing dyes which is difficult to treat.

Efficient catalysis for the treatment of dyes in waste water is necessary. Promising approaches involve the degradation of organic dyes using photo catalyst ( $\text{TiO}_2$  nanoparticles) and microorganism (white rot fungi) or their secreted enzymes.

a) Photo Catalytic dye degradation  
 It is the advanced oxidation process for breaking down organic pollutants. This process involves the attack and destruction of organic pollutants by reactive species such as hydroxyl radicals ( $\text{HO}^{\cdot}$ ) and holes ( $\text{h}^{\cdot}$ ).  
 The metal oxide nano particles are excited to generate electron-hole pairs under irradiation and the photogenerated carriers can be formed and then interact with the dye molecules leading to the decomposition of dye into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

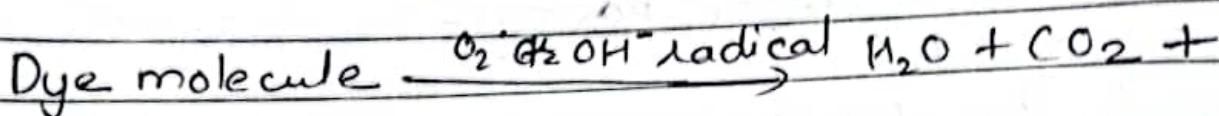
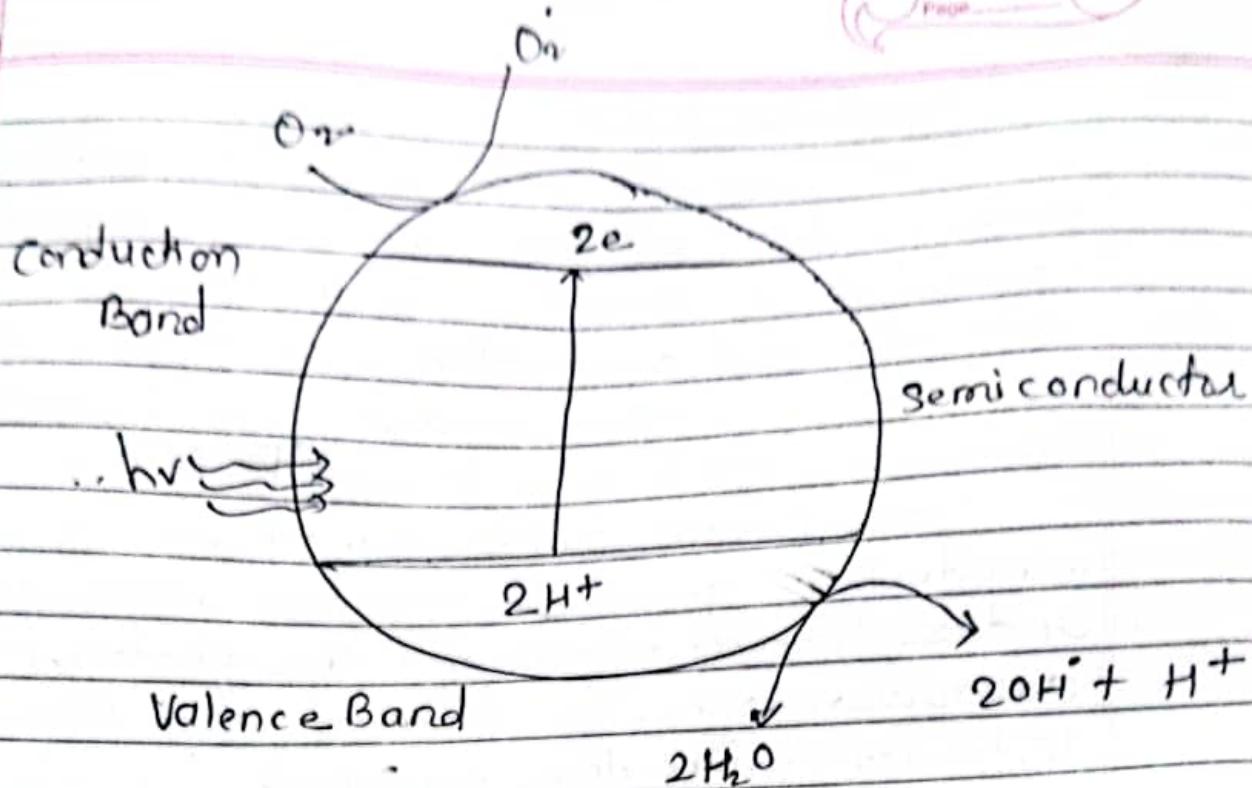
The mechanism of dye catalytic degradation can be explained taking and example  $\text{ZnO}$ .

Steps :

- I Activation of  $\text{ZnO}$  by UV light.
- $$\text{ZnO} + \text{hv} \longrightarrow e^- + \text{h}^{\cdot}$$
- $$e^- + \text{O}_2 \longrightarrow \text{O}_2^{\cdot}$$

- II the oxidative and reductive reaction:
- $$\text{O}_2^{\cdot} + \text{H}^+ \longrightarrow \text{HO}_2$$
- $$2\text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$$
- $$\text{H}_2\text{O}_2 + \text{O}_2^{\cdot} \longrightarrow \text{HO}^{\cdot} + \text{O}_2 + \text{OH}^-$$
- $$\text{HO}^{\cdot} + \text{organic dyes} \longrightarrow \text{CO}_2 + \text{H}_2$$

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degraded product

fig: Catalytic dye degradation using  
semi-conductor catalysis.

Some examples of commonly used commercial catalyst in dye degradation are:  $TiO_2$ ,  $SnO_2$ ,  $ZnO$ , Graphene-gold nanocomposite,  $Ag-ZnO$  composite.

### b) Bio-catalytic degradation:

Bio-catalyst play a crucial role in the degradation of dyes either directly or indirectly through metabolic process. Example of such enzymes includes peroxidase, lignin peroxidase, manganese peroxidase, azo reductase, laccases, etc.

Algae also play a significant role in dye degradation through biosorption and biodegradation.

Biosorption involves the transfer of dye constituents from the liquid to the solid phase such as from water to the surface of algae.

Biodegradation involves breaking the chemical bonds in dye structures. Various algal species such as macroalgae *Enteromorpha* sp. for degrading C.I Basic Red 46, *Shawnelia* algae (SAL) for acid Red 27, and the green macroalgae *Cladophora* sp. for treating Malachite Green have been reported for their ability to biodegrade azo-dyes.

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## Selection Criteria of Catalyst

Various factors must be taken into account during the catalyst selection process:

1. **Activity**  $\Rightarrow$  A catalytic material should possess high level of activity. The activity of a catalytic material depends on the nature of the active sites, often related to electronic and geometric effects influencing the chemisorption process of the reactants. Having a large specific surface area with right active sites results in the higher activity.

2. **Volumetric Efficiency**  $\Rightarrow$  High volumetric efficiency indicates that the catalyst is effectively utilizing its volume leading to the effective conversion of reactant.

3. **Selectivity**  $\Rightarrow$  Selectivity refers to the obtaining exclusive or large proportion of the desired product. In heterogeneous catalysis, selectivity relies on chemisorption characteristics, such as dissociative or non-dissociative process and competitive adsorption on the sites.

4. **Stability**  $\Rightarrow$  The stability of catalyst is revealed in different forms such as  
a) Thermal stability (resistance to heat treatment)

- (B)
- b. Hydrothermal (resistance to treatment including water or steam)
  - c. Chemical stability (resistance to chemical treatments)
  - d. Mechanical stability (mechanical strength).
- e. Regeneration  $\Rightarrow$  certain poisons or foulants can be selectively eliminated through chemical washing, mechanical treatments, heat treatments or oxidation. The regeneration and reuse are typically preferred.

6. Cost  $\Rightarrow$  The catalytic materials should be affordable and accessible. The cost of reagent is influenced by elemental, composition, purity and synthesis procedure.

7. Environmental impact  $\Rightarrow$  Sustainable catalysts are favoured as they adhere to green chemistry principle by minimising the usage of harmful compounds and lowering pollutant emissions. The emphasis is on the catalyst that contribute to energy efficiency, makes use of renewable resources and feedstock.

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## Catalyst Design Criteria

The distinct steps in the method of designing of catalyst are shown in table below.

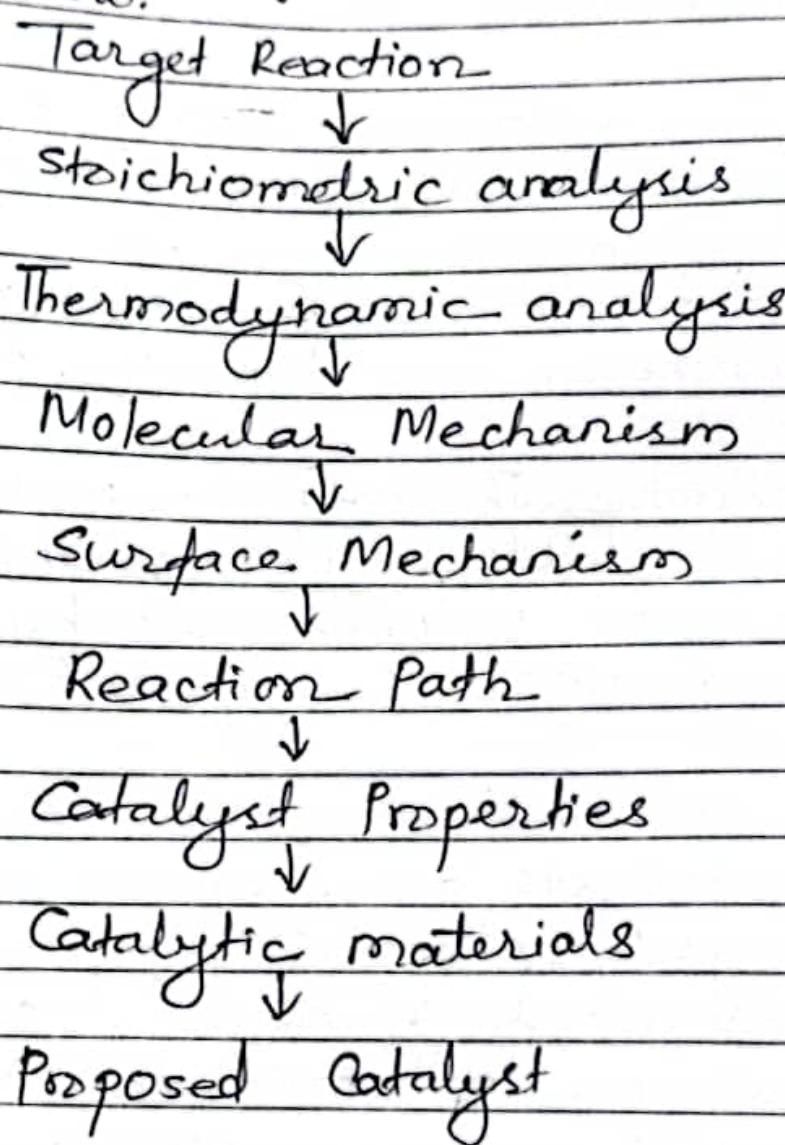


fig: Steps in catalyst design.

a) Target reaction:

Designing of catalyst begins with setting of target reaction



$$\Delta H = -76.8 \text{ kcal/mol}^{-1} \text{ at } n=2n.9$$

Q) Partial oxidation to formaldehyde is a worthy process which requires catalyst with high activity & selectivity.

### 1) Stoichiometric Analysis:

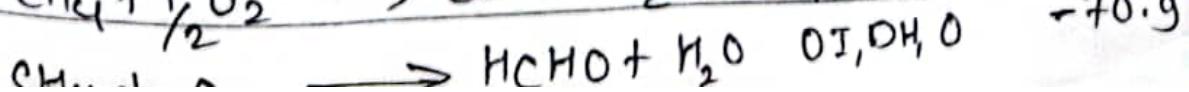
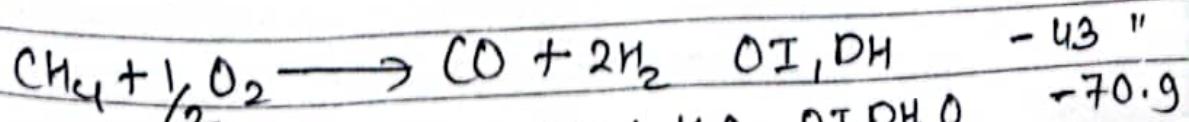
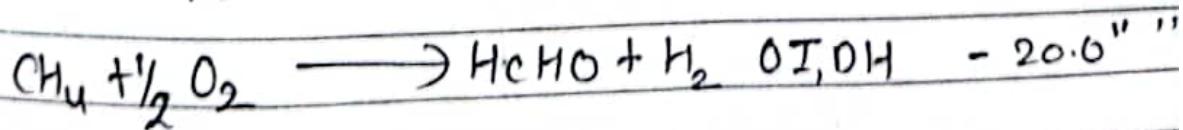
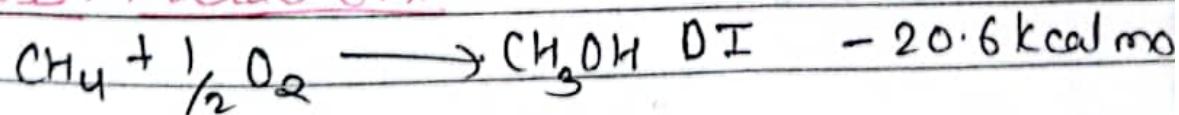
In this step three tasks are undertaken. Initially all potential stoichiometric chemical equations are compiled and organized logically including primary reactants, reactant self-interaction, reactant cross interaction, reactant product interaction and product product interaction. These seven is categorized as dehydrogenation (DH), Hydrogenation (H), oxidation (O), oxygen insertion (OI), dehydration (DW) and group Addition (A).

#### Interaction type

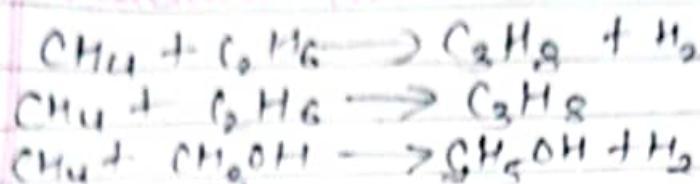
##### self Interaction

Reaction	Category	$\Delta H_f^\circ \text{ at } 500^\circ \text{C}$
$2\text{CH}_4 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2$	DH	8.5 kcal/mol
$2\text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2$	DH	12.8 "
$2\text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + 3\text{H}_2$	DH	22.2 "
$2\text{O}_2 \rightarrow \text{none}$		

#### Cross - interaction.



### Reactant - product reactions:



DH, A

A

DH, A

16.6 kcal/mol

4.5 kcal/mol

10.5 "

### c) Thermodynamic analysis:

The goals in this stage involve evaluating the thermodynamic feasibility of each stoichiometric equation and categorising them into groups with similar chemical functions.

Reactions with Gibbs free energy change ( $\Delta h$ ) values exceeding  $10 \text{ kcal mol}^{-1}$  are not considered here as the reaction becomes unfavourable to proceed.

### d) Proposed Molecular Mechanism:

The aim of this stage is to conceptualize the molecular process. Discernment is required to distinguish among various competing possibilities.

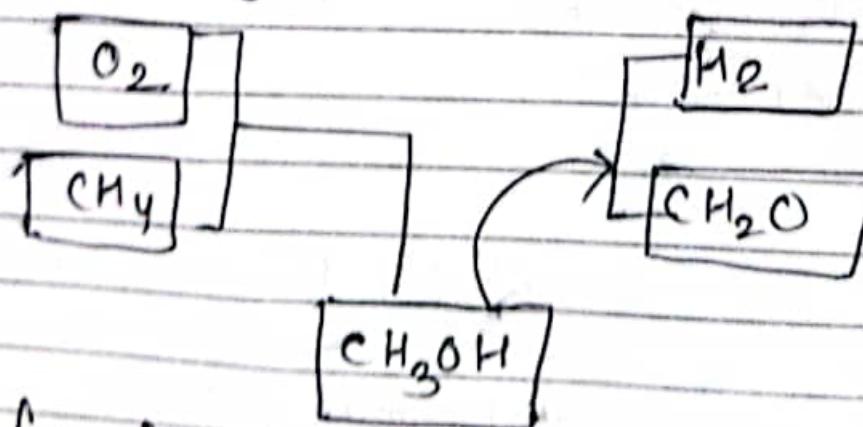


fig: Proposed molecular mechanism of partial oxidation of  $\text{CH}_4$ .

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### c. Proposed Surface Mechanism.

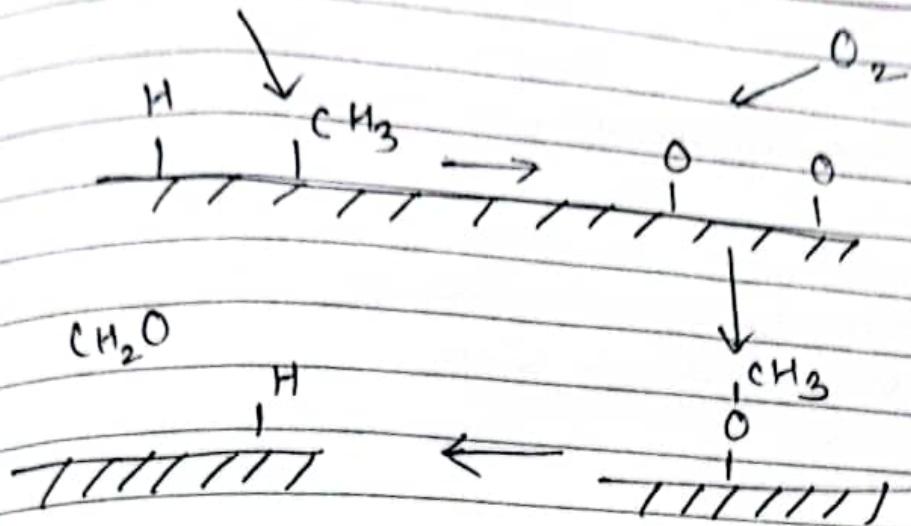


fig: Surface mechanism for formaldehyde formation.

oxygen adsorbs as molecular ion or atomic species, with the latter being preferred since the product contains only one oxygen. However, adsorbed oxygen atoms are reactive and lead to oxidation. To prevent oxidation, it is necessary that oxygen dissociation produces chemisorbed bond too strong for migration. This implies that the adsorbed  $\text{CH}_3$  must be mobile enough to diffuse to oxygen sites.

### e) Reaction Path identification:

The required reaction pathways have been defined at this point. The catalyst should encourage oxygen insertion and moderate dehydrogenation while discouraging intense oxidation and dehydrogenation.

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### Necessary Catalyst Properties:

The catalyst must possess:

- i) sites for adsorption leading to dissociation and the formation of immobile oxygen species.
- ii) sites for mild dehydrogenation.
- iii) Proximity of sites to facilitate final dehydrogenation step.

### Renewable Energy Catalyst:

Catalysts play a fundamental role in the sustainable chemistry, as catalysts have the potential to enhance process efficiency, decrease greenhouse gas emissions and reduce waste generation. The process involves utilizing renewable energy to split water into hydrogen and oxygen. Photocatalytic and electrocatalytic water splitting plays a key role in establishing the groundwork for a clean and sustainable energy society.

### Electrocatalyst and Electrocatalysis:

Electrocatalyst refers to a type of electrode material that interacts with specific species during a faradaic reaction (flow of current is equal to electricity passed) without undergoing

any change in itself electrocatalysis are typically heterogeneous catalysis, which implies that the reaction occurs on the surface of the catalyst.

An effective electrocatalyst is characterized by its ability to exhibit a high current density at a low overpotential.

Currently, leading electrocatalyst for water splitting in acidic environment are  $\text{IrO}_2$  and  $\text{RuO}_2$  for the oxygen evolution reaction (OER) and Pt for hydrogen evolution reaction (HER).

This process involves the hydrogen evolution reaction (HER) at cathode producing  $\text{H}_2$  gas, and the oxygen evolution reaction (rOER) at anode yielding oxygen gas.

To mitigate losses in charge transport during electrochemical process, conventional water electrolysis is commonly conducted either in acidic environment utilizing a proton exchange membrane (PEM) or alkaline setting with a diaphragm.

Under standard condition achieving electrochemical water splitting requires a cell voltage of 1.23 V corresponding to an energy input of  $\Delta H = 237.7 \text{ kJ/mol}$

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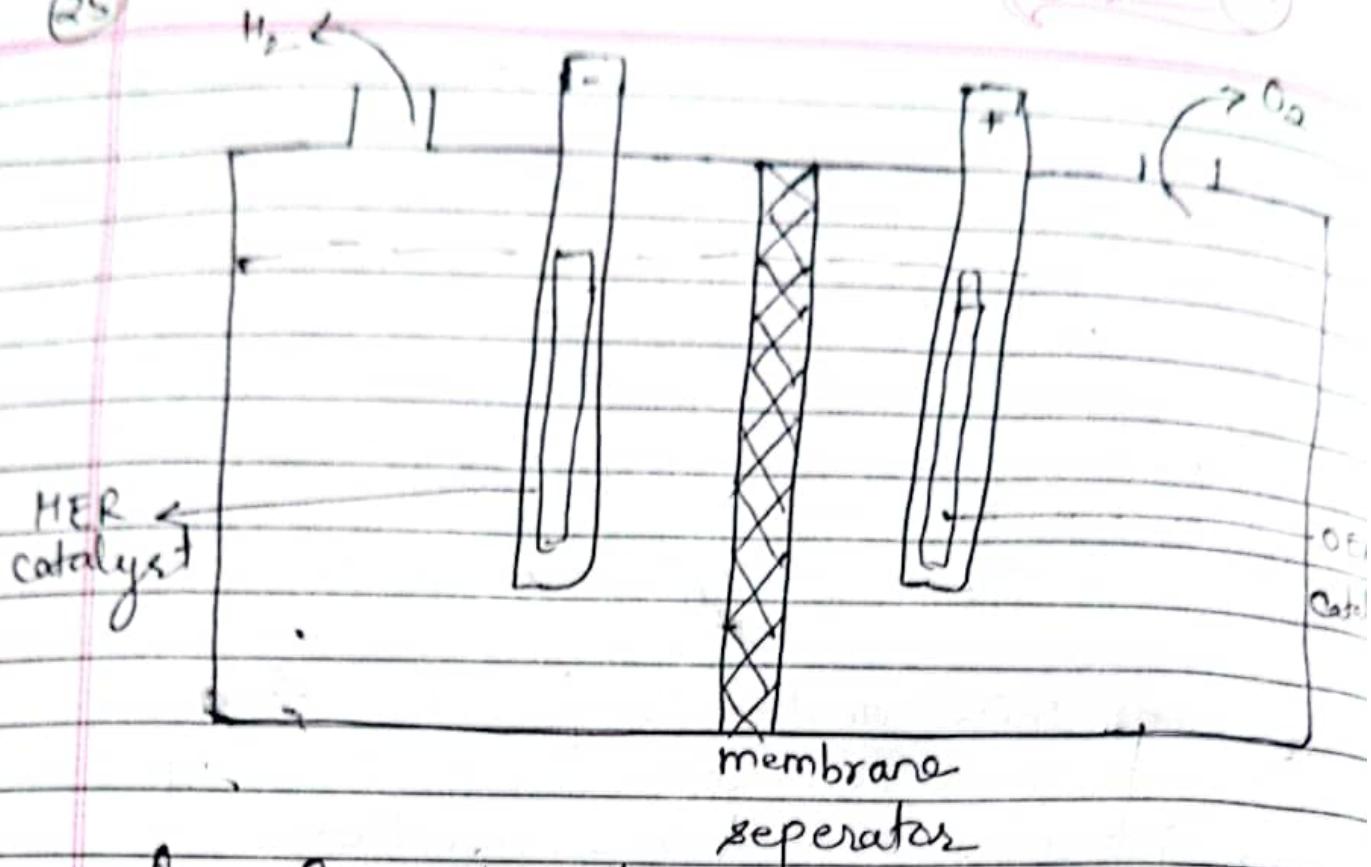
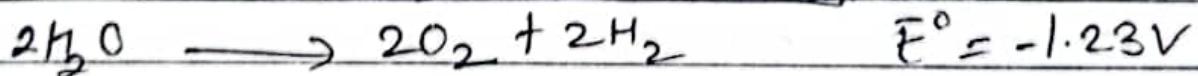
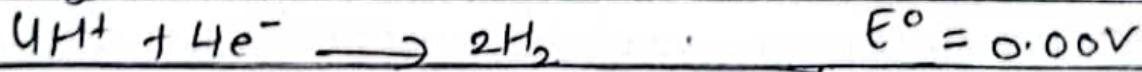
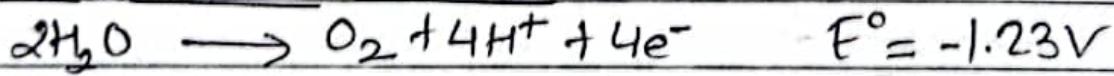
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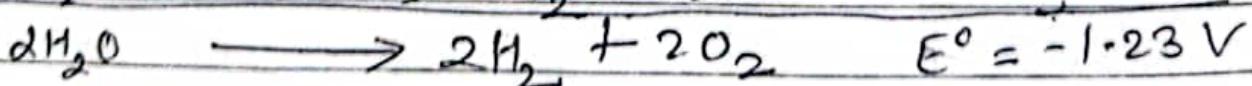
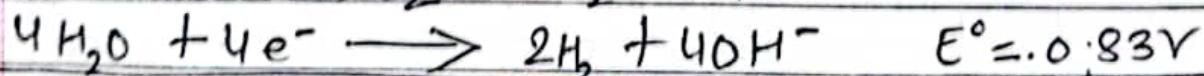
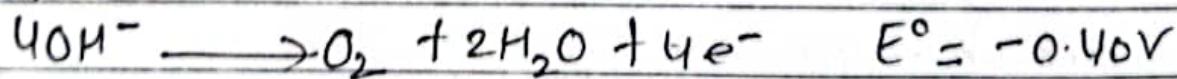
fig: Conventional water electrolyzer.

The efficacy of electrocatalyst to facilitate the hydrogen evolution reaction (HER) is significantly determined by the strength of Me-H bond.

In acidic solution:-



In alkaline solution.



## Photo Catalyst & photocatalysis.

\* Photo catalysis utilizes photonic energy ( $h\nu$ ) as a driving force to bring the chemical transformation. It involves the electro reorganization to break / create chemical bond.

The material which induces and accelerates the rate of chemical reaction under photo-irradiation is called photo-catalyst. And the catalytic process which is accelerated by the absorption of photon is called photo-catalysis.

e.g. Photo-catalytic water splitting into hydrogen and oxygen using light energy (Redox reaction).

The potential required for splitting is 1.23V.

Process : If the photonic energy ( $h\nu$ ) is greater than energy difference between valence band (energy range comprising the electrons of outermost shell of an atom in ground state) and conduction band (band of energy level consists of electron in an energized atom) then it leads to excitation of electron from valence band and conduction band. This emf is responsible for the hydrogen evolution reaction (HER) and

~~oxygen evolution reaction (OER) in aqueous medium.~~

- ~~six gears of overall water splitting~~
1. Absorption of photon
  2. Separation of  $e^-$ ,  
carrier diffusion
  3. Carrier transport
  4. Catalytic efficiency.
  5. Mass transfer of reactant & Product.
  6. Mass transfer of excitons and diffusion.  
*Note: Separation of excitons and diffusion carrier take place simultaneously  
and coherently).*

Photon absorption generates an excitation of electron from Valence band to conduction band. The femto second ( $f\text{m}$ ) process leads to the relaxation of electron and hole at Conduction band.

Similarly electron hole pair is separated in femto to pico seconds into free carriers.

The semi-conductor catalyst guides the electron and the hole to hydrogen evolution reaction (HER) and OER (oxygen evolution reaction).

Water splitting is a redox process where proton undergo reduction to form  $H_2$  while water undergo oxidation reduction to form  $O_2$ .

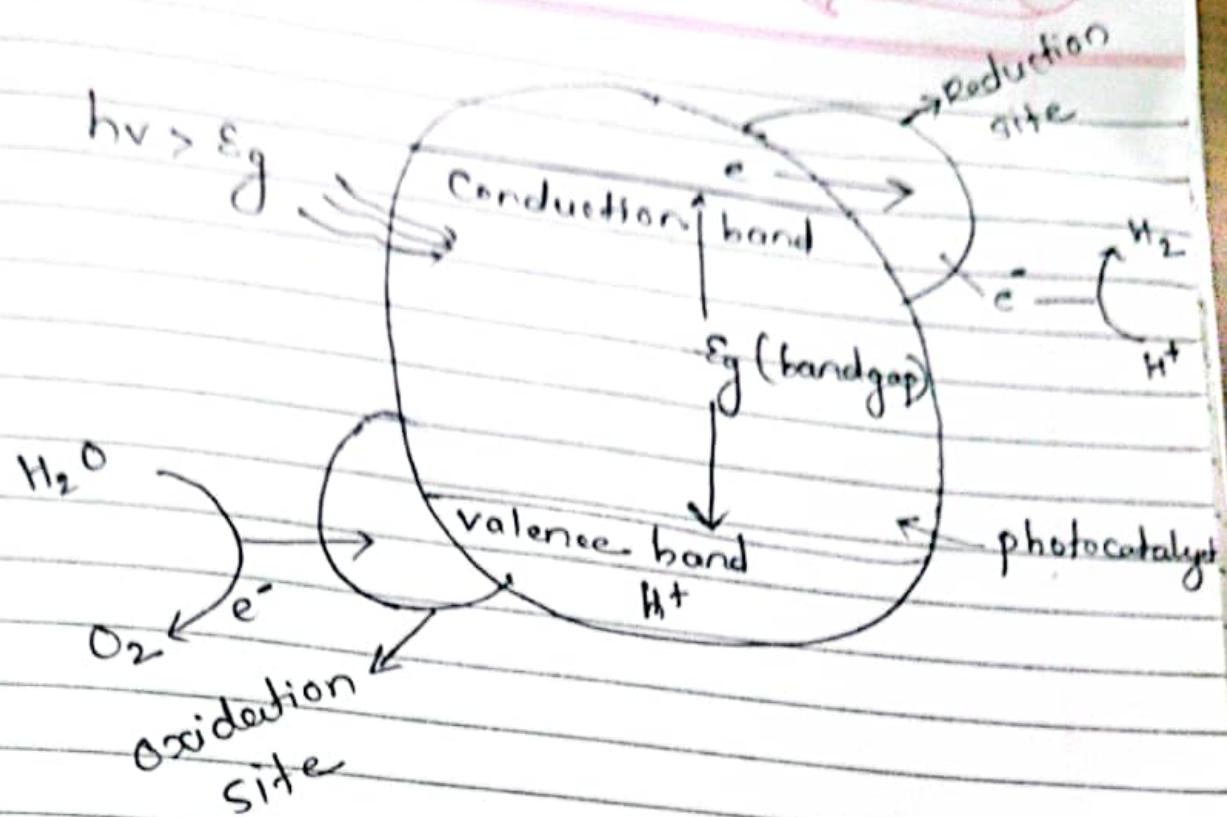
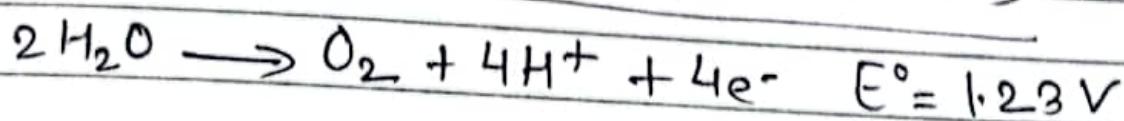


fig:- Schematic Energy diagram of photo-catalytic water splitting by photoexcitation system.

Reaction. (At Valence band  $\rightarrow$  Oxidation)



At Conduction band (reduction)

