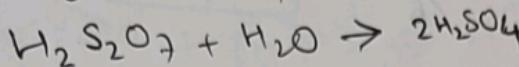
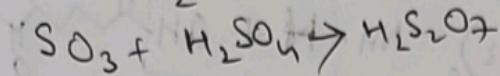
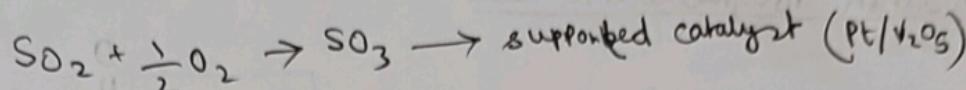
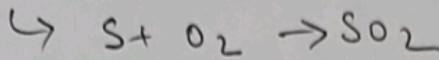


8/08/23 Prof. B.B.

## H<sub>2</sub>SO<sub>4</sub> manufacturing

i) Chamber Process

ii) Contact Process



P.E.

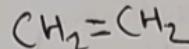
Monomeric unit

↓  
Dimer

↓  
Trimer

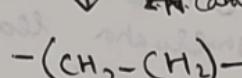
↓  
Tetramer

↓  
Polymer



Monomeric unit

↓  
60-100 atm, 70°C  
Z.N. Catalyst



n = no. of repeat unit

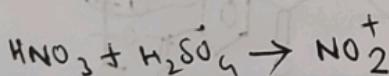
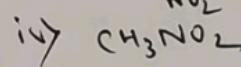
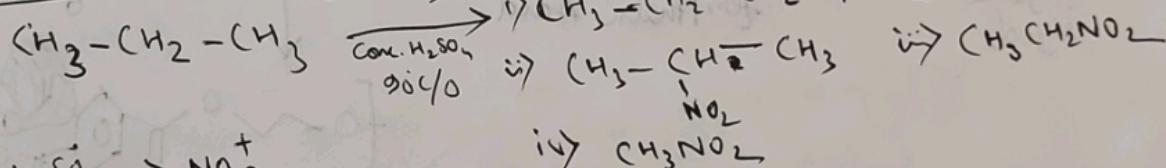
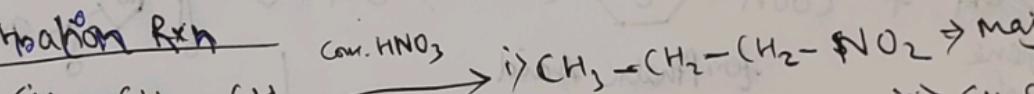
Z.N. Catalyst

Zigler-Natta catalyst

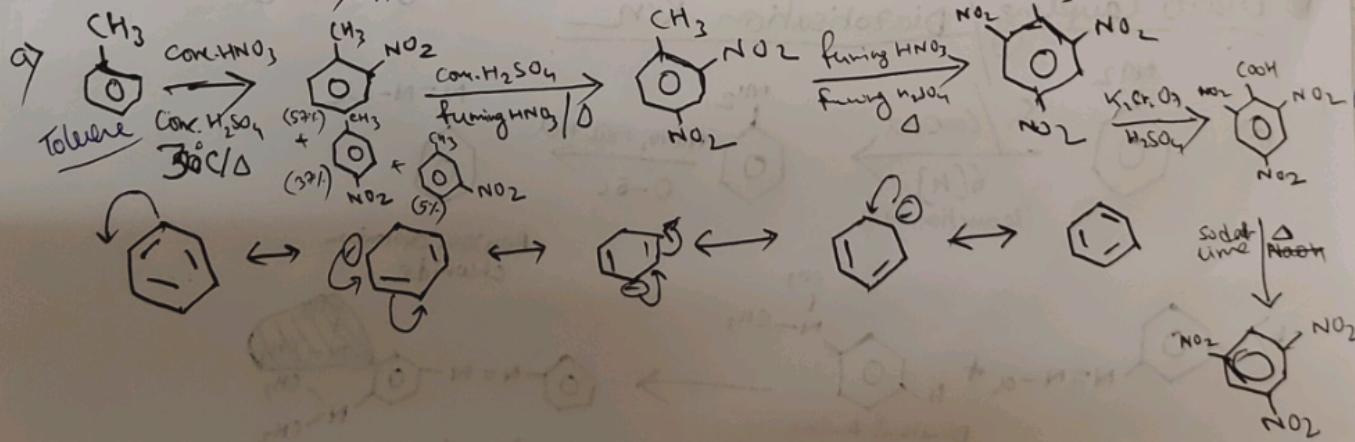
TiCl<sub>4</sub> + Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>

C<sub>2</sub>H<sub>5</sub>  
C<sub>2</sub>H<sub>5</sub>  
C<sub>2</sub>H<sub>5</sub>

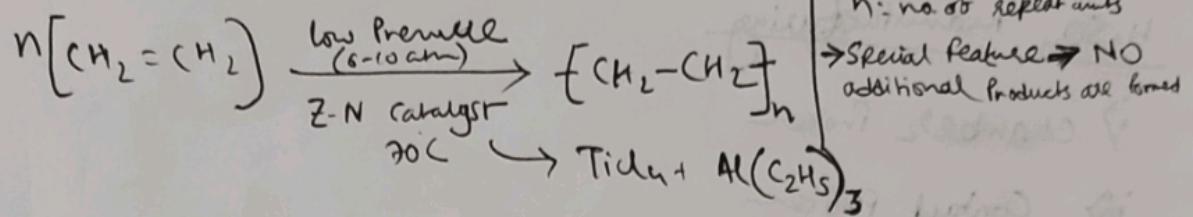
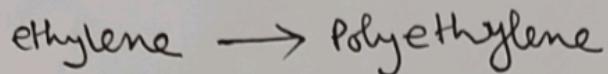
## Nitration Rxn



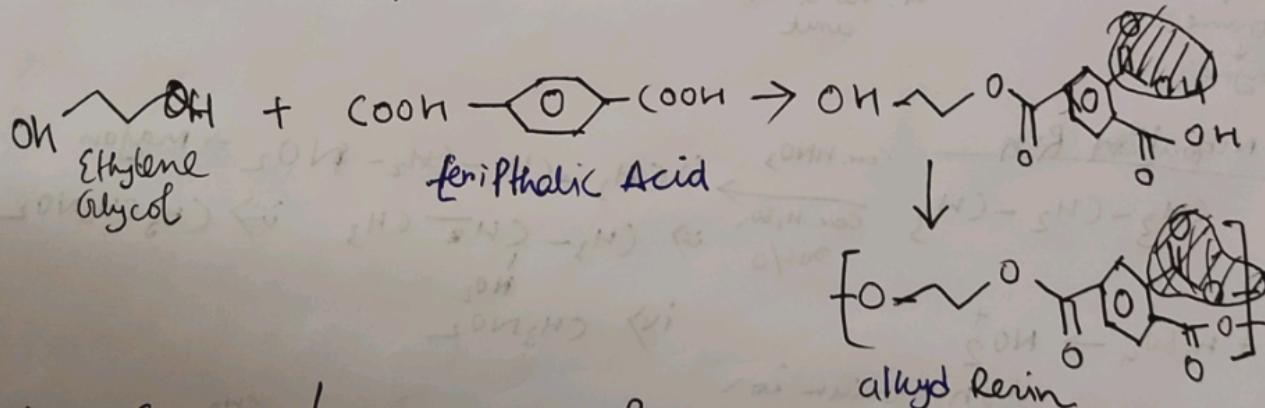
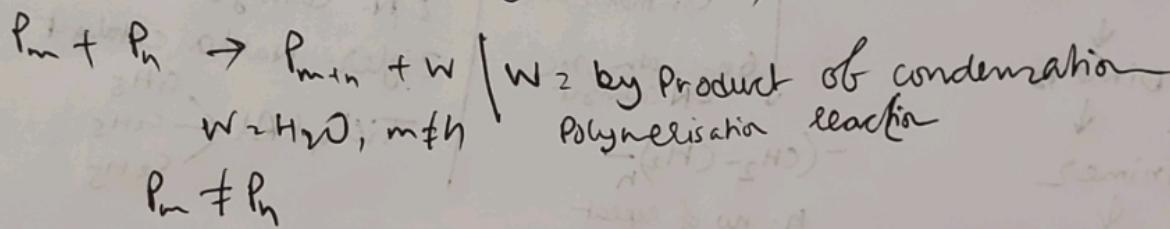
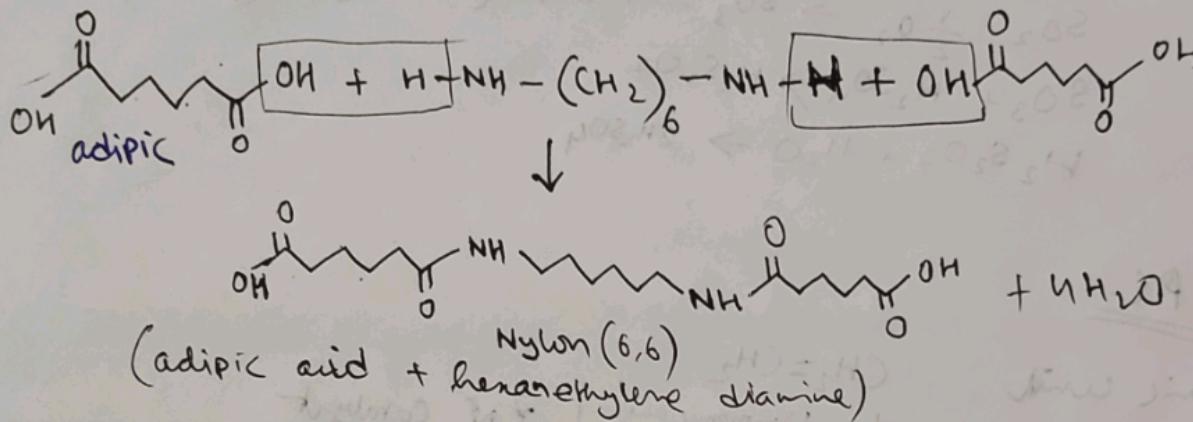
nitronium ion



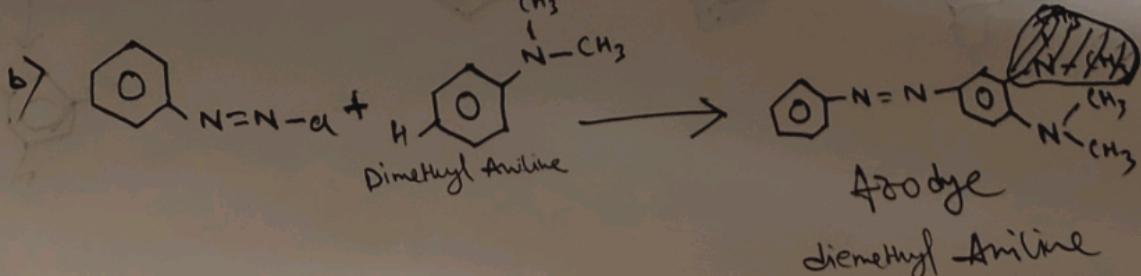
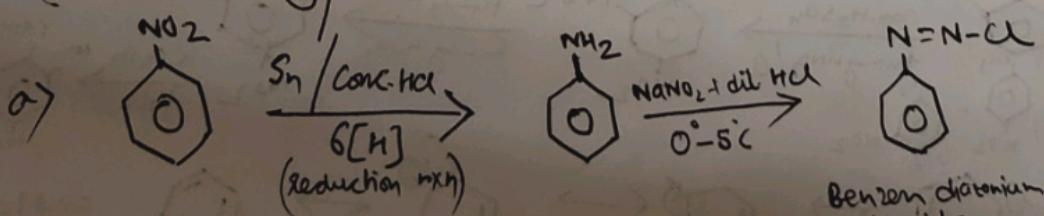
## ② Additional Polymerization



## ③ Condensation Polymerisation

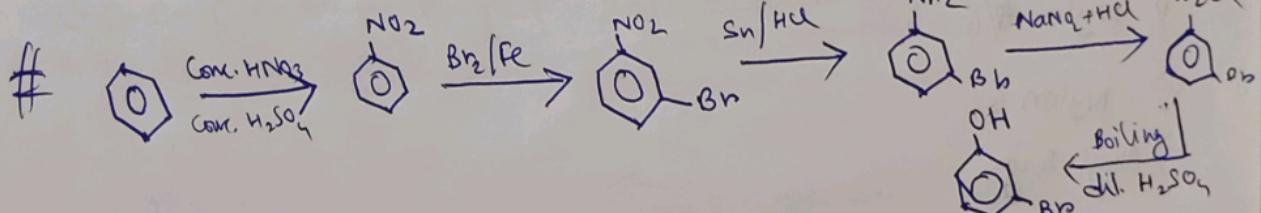
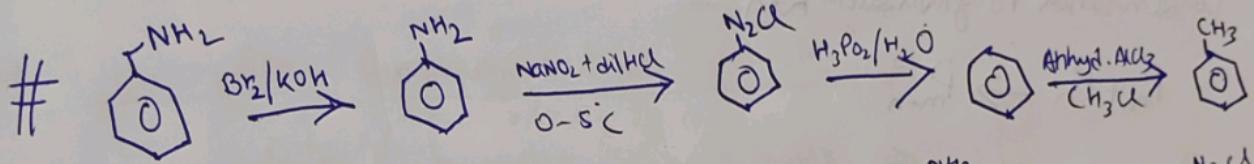
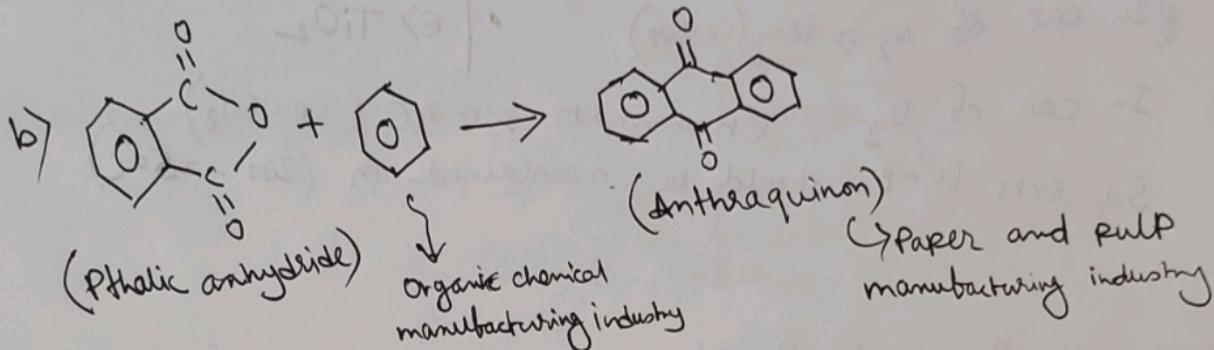
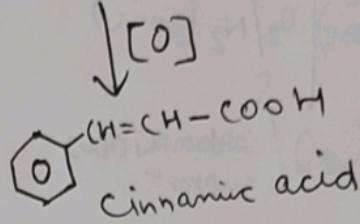
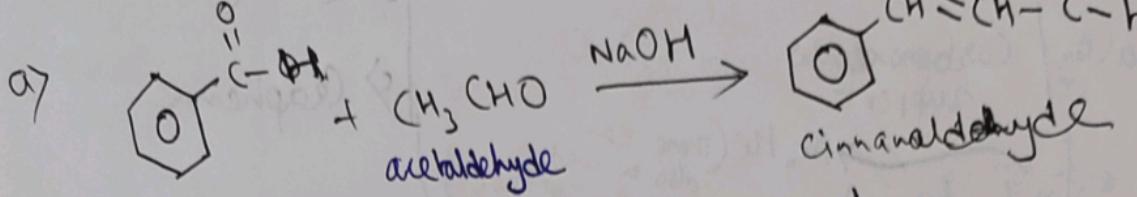


## ④ Diazo Coupling / Diazotisation Rxn

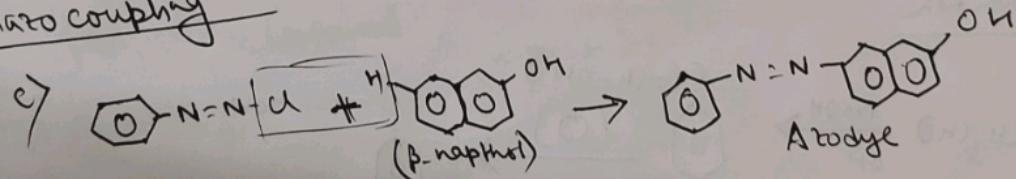


This reaction is used in dye manufacturing industries.

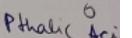
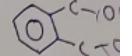
### Condensation Reaction



### Diazo coupling



## Dehydration



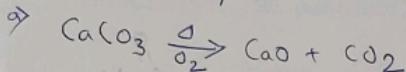
## Calcination

Supporting Agent

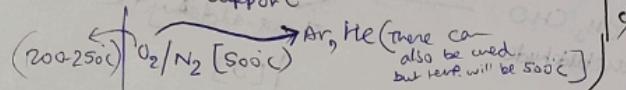
Carbonaceous

Solidify & dry  
22 PH40098  
Starting Diggidn. 112.

## Calcination / Decomposition Rxn



b)  $\text{CaCO}_3$  / Carbonaceous support



CaO / carbonaceous support

In case of  $\text{N}_2 \rightarrow \text{len}(\text{CO+CO}_2)$ .

In case of  $\text{O}_2$ , environment  $\rightarrow$  more ( $\text{CO+CO}_2$ ).

So, rxn temp. should be maintained in (200-250°C).

## Carbonaceous supports -

a) Activated Carbon

b) CNTs (Carbon Nano tube)

c) Graphene

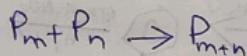
## Non-Carbonaceous supports -

a)  $\text{Al}_2\text{O}_3$  b)  $\text{SiO}_2$ ,

c)  $\text{SiO}_2 - \text{Al}_2\text{O}_3$  d)  $\text{ZnO}_2$

e)  $\text{TiO}_2$

## Condensation Polymerisation Rxn:

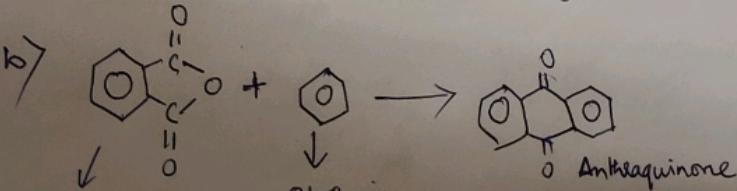
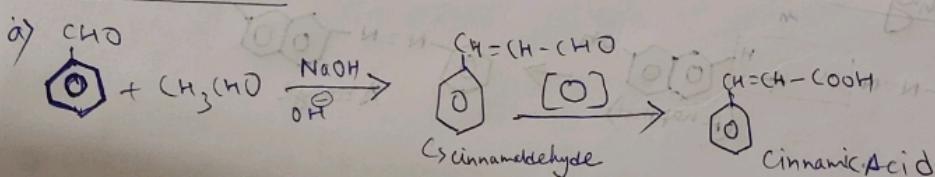


Nylon 6/6

Nylon 6

Alkyl Resin

## Condensation Rxn



Paper and pulp manufacturing industry.

## Cyclization

-C=C-C-

n-Paraffins

-C=C-C-

Naph

iii Aromat

iv t - Pa

v Hydrog

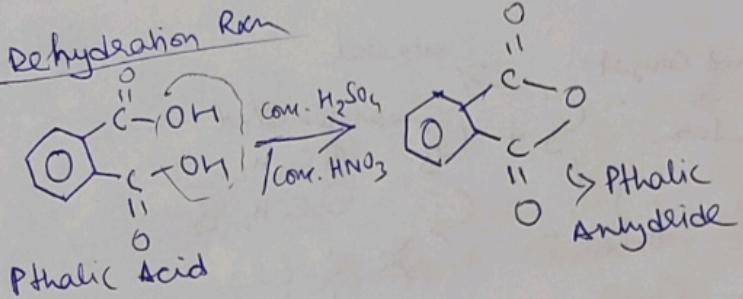
## Paraffin

-C-C-C-

n-Paraf

dye industry  $\rightarrow$  azo  
Paper and Pulp: Anthraquinone

### Dehydration Rxn

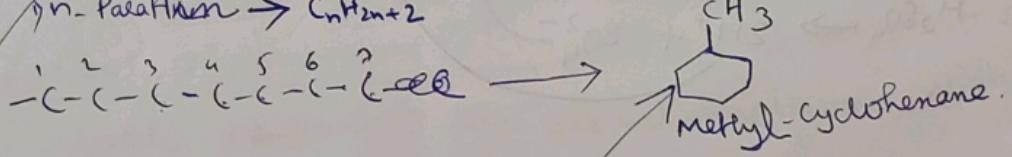
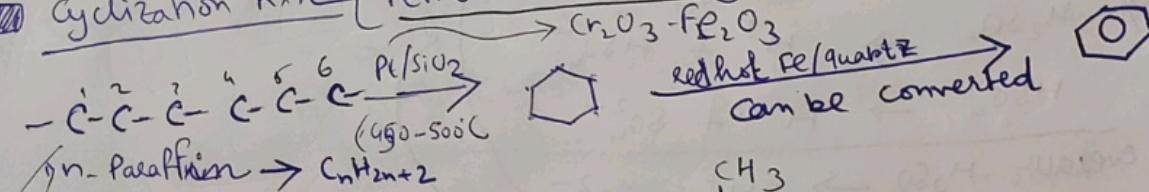


### Calcination

supporting Agent:  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$   $\rightarrow$  zirconia  
 $\rightarrow$  non-carbonaceous support  
 $\rightarrow$  Tiatenia

Carbonaceous support  $\rightarrow$  Activated carbon  
 $\rightarrow$  CNTs  
 $\rightarrow$  Graphene

### Cyclization Rxn [Petroleum Refinery industry]



i) Naphthalene Compound

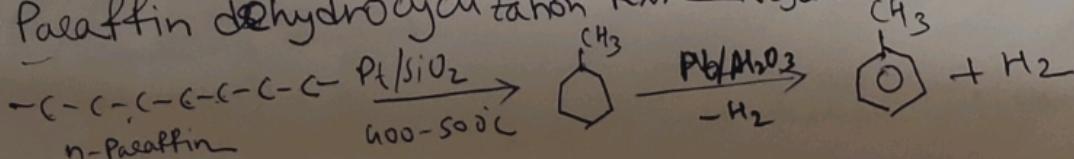
ii) Aromatic Compound

iii) t-Paraffine Compound

iv) Hydrogen

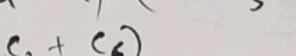
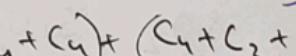
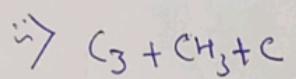
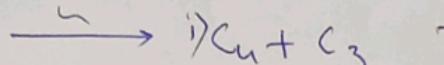
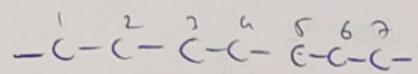
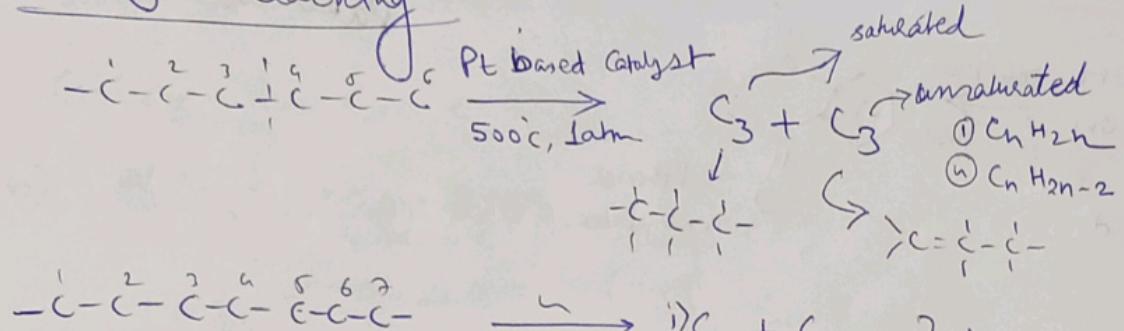
cyclic compound,  
without  $=\text{}$

### Paraffin dehydrocyclization Rxn $\xrightarrow{\text{Catalyst}}$ cyclization Rxn -

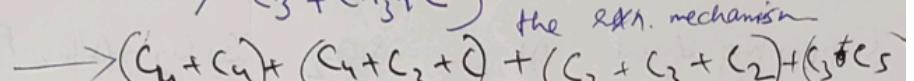
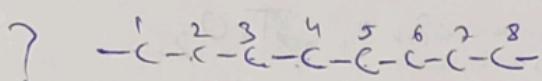


dehydrogenation [removal of  $\text{H}_2$ ]

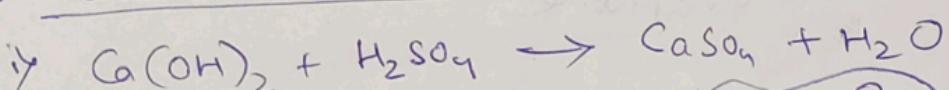
## Catalytic Cracking



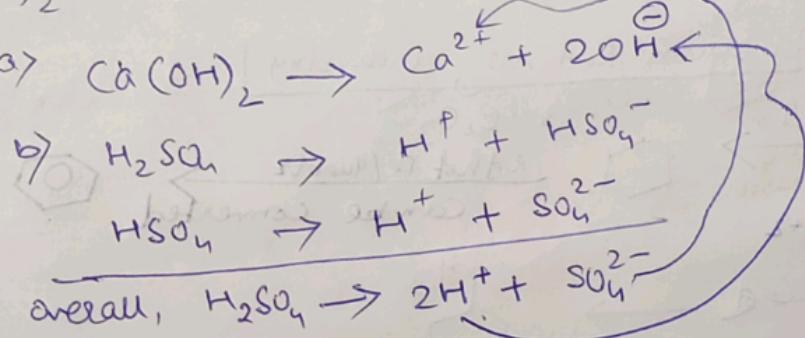
The saturated unsaturated compound depends upon the R.A. mechanism



## Double Composition Rxn (cement manufacturing eng.)

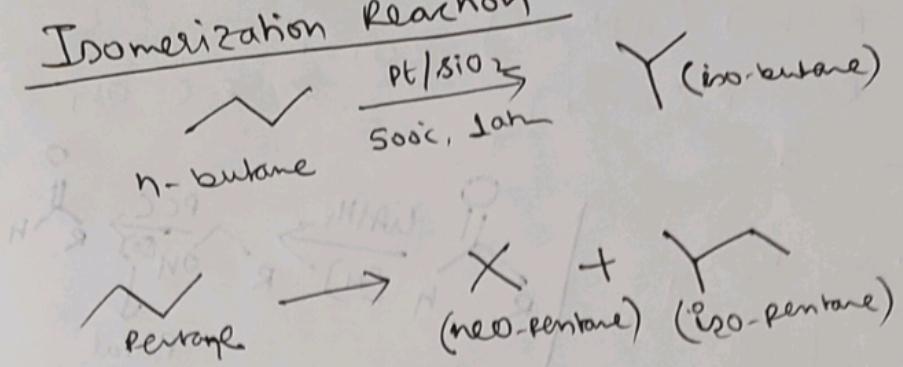


Why the  
name is  
double  
decomposition



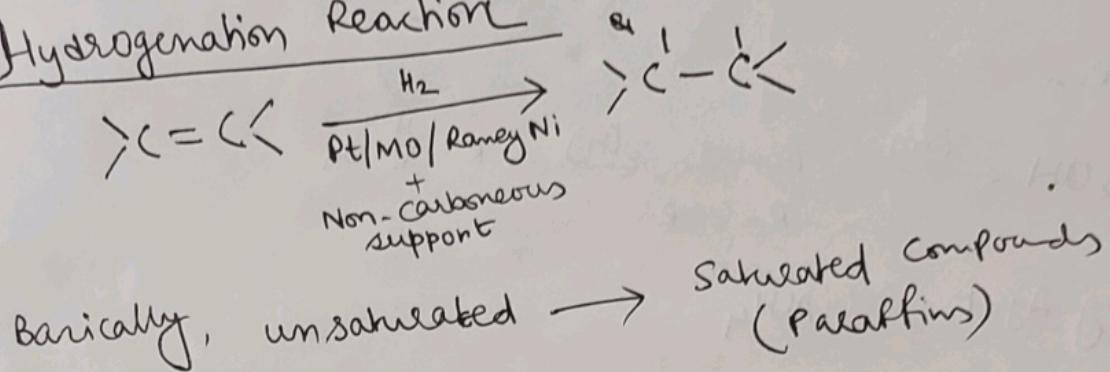
21st Aug, Prob B.B.

### Isomerization Reaction

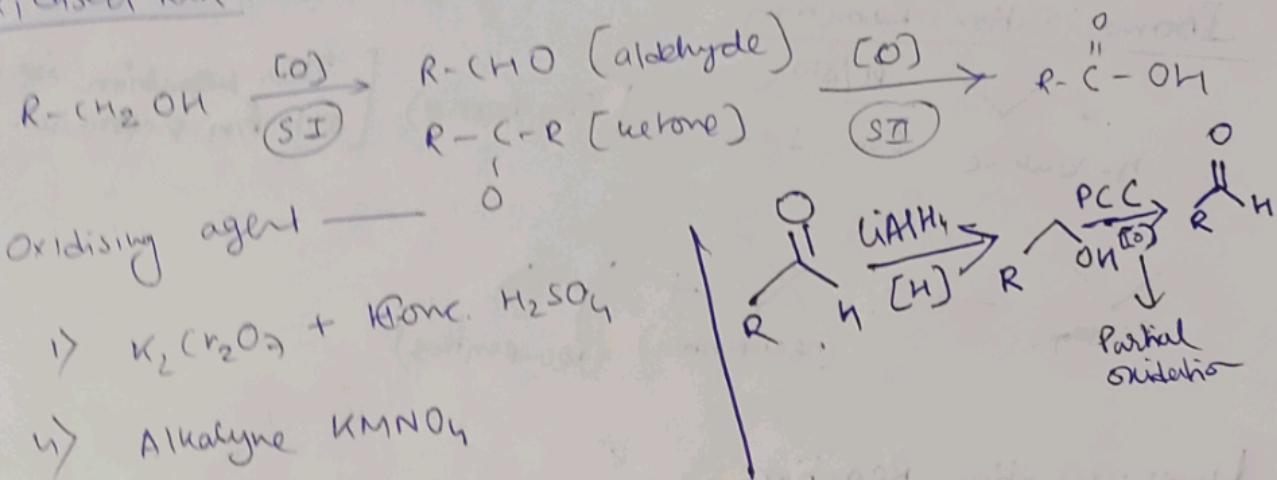


[This reaction is carried out in the petroleum industry]

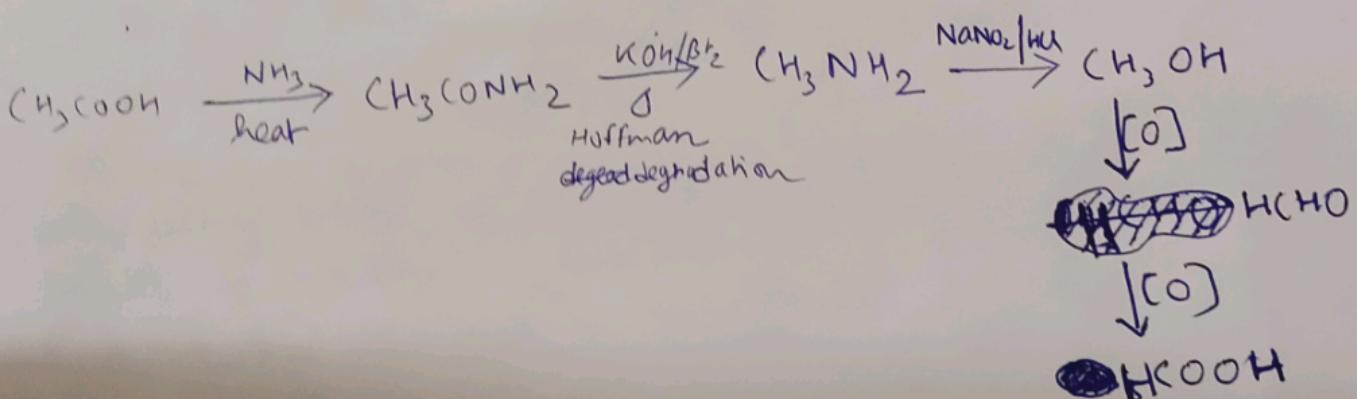
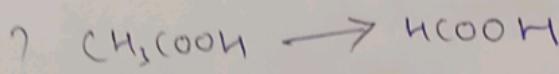
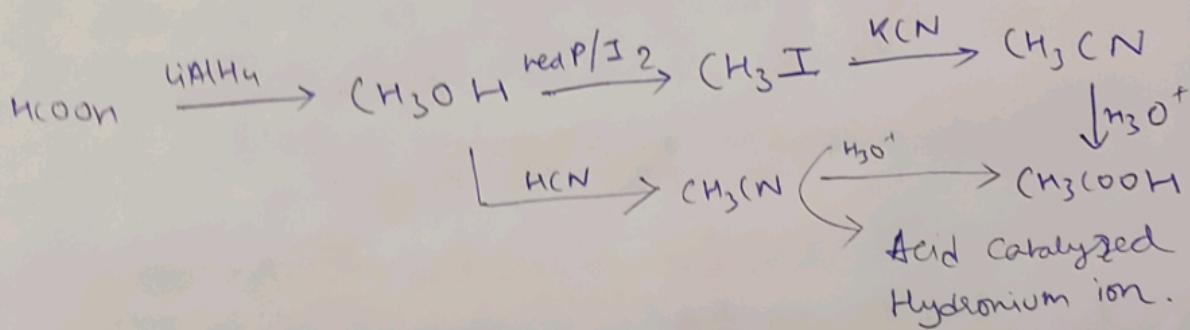
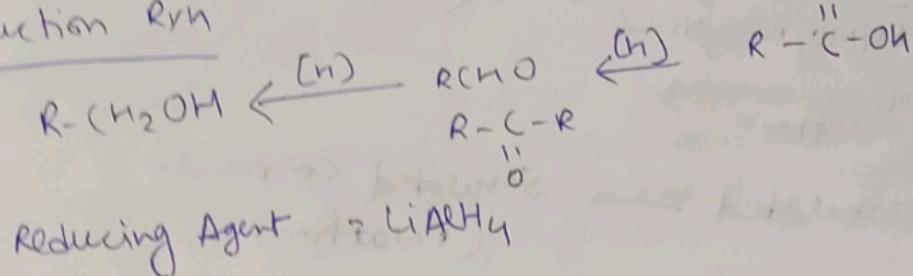
### Hydrogenation Reaction



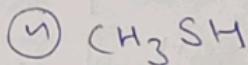
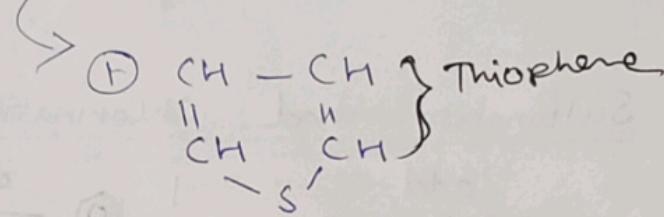
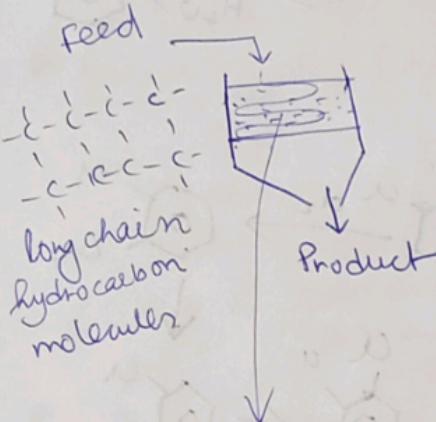
## Oxidised Rxn



## Reduction Rxn



# Hydrolytic Hydrodesulfurization Rxn  
 Removal of sulphur compounds.



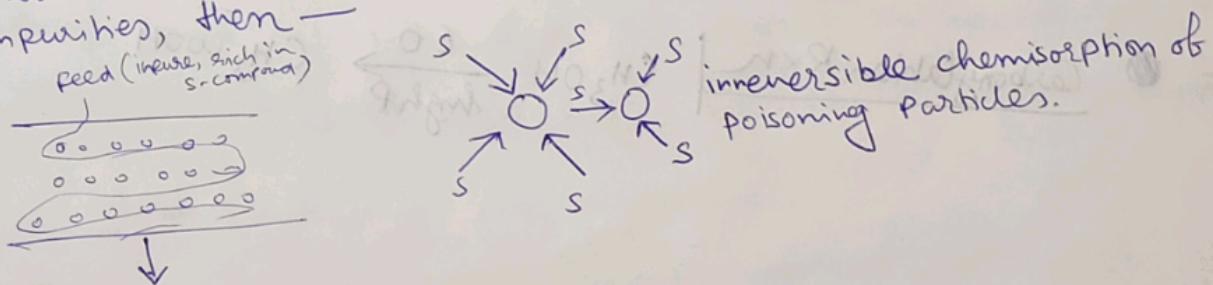
→ methyl mercaptan.

If there is powder form in fixed bed —

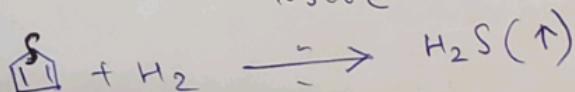
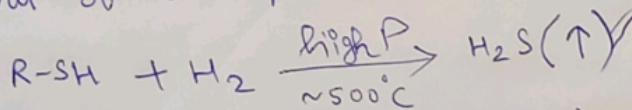
Product will be  $\Rightarrow$  Product + Catalyst + unconverted feed.

But if the fixed bed is pellet ( $\sim 3\text{ mm diameter}$ ), then we will get only Product.

Now, if feed is not pure and contain S-compounds as impurities, then —



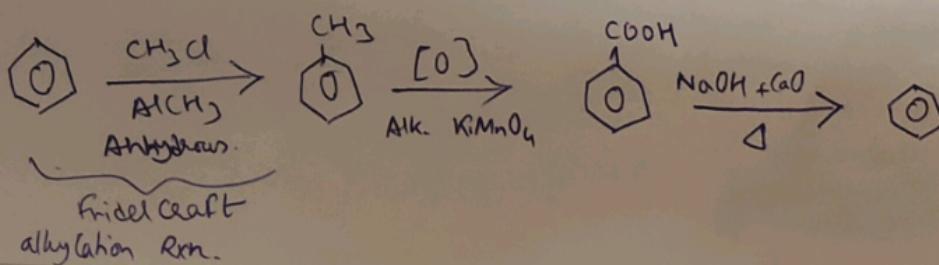
Removal of S-compounds —

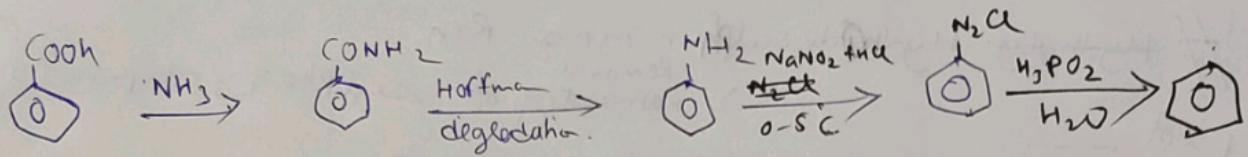


# Carbonylation and Decarbonylation Rxn

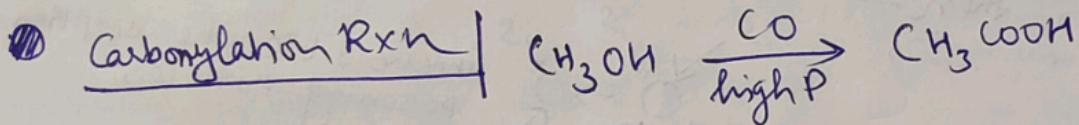
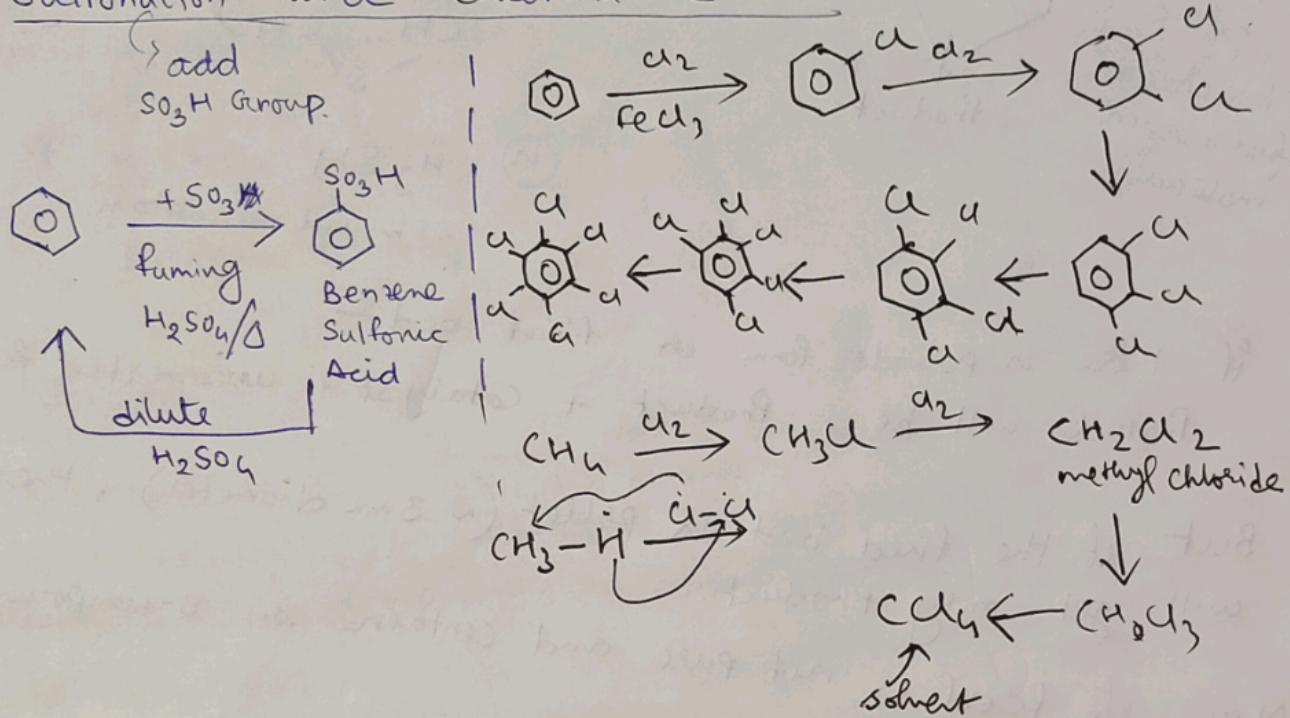
$(\text{COOH})$  remove  $-\text{COOH}$  group.

[Organic chemicals manufacturing industries remake use of carbonylation and decarbonylation rxn.]





## # Sulfonation and Chlorination Rxn



29th Aug, B.B.

Pores in support →

- **Micro Pores ( $< 2\text{nm}$ )**
- **Meso Pores ( $2\text{-}50\text{nm}$ )**
- **Micropores ( $> 50\text{nm}$ )**

# BET surface area analysis helps to determine pore diameter

surface acidity / basicity

Feed:  $\text{CO}_2/\text{H}_2$  (for surface basicity measurement)

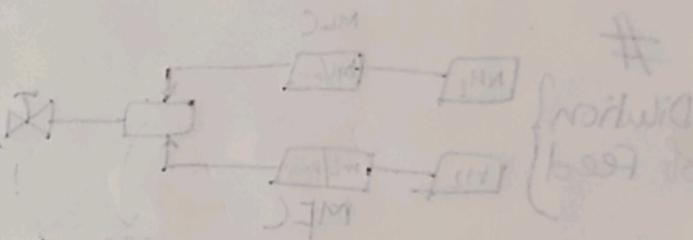
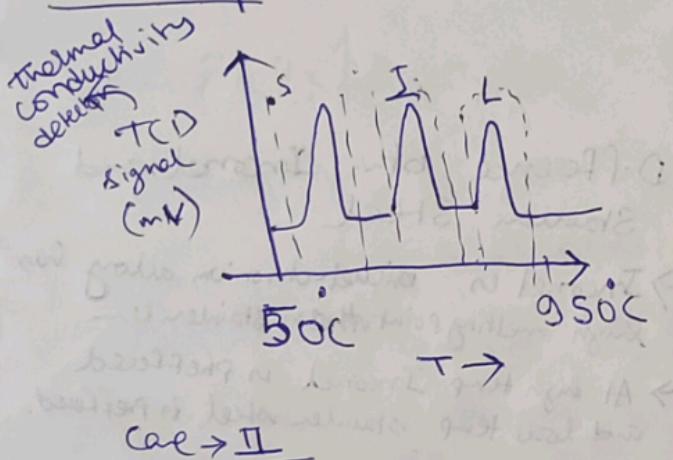
Y Feed/probe gas ( $\text{NH}_3/\text{H}_2$ ) for surface acidity measurement

a) low T → strong acidic functional groups.

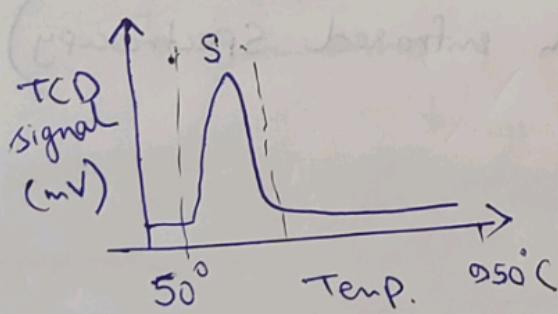
b) Intermediate T → intermediate acidic func' groups.

c) High T → low acidic functional groups.

Case - I Existence Extent of S.I., low acidic functional groups.



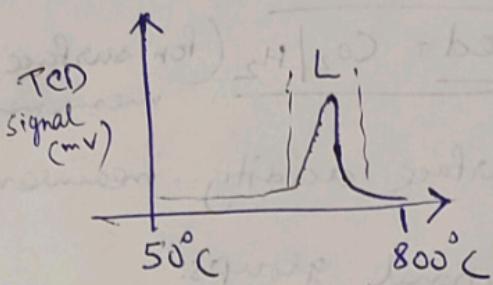
Case - II  
Existence of Strong acidic func. group.



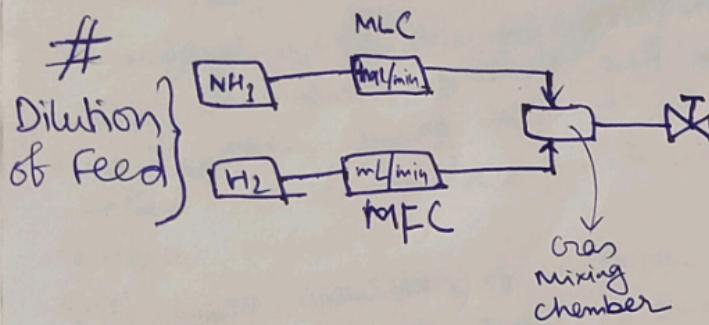
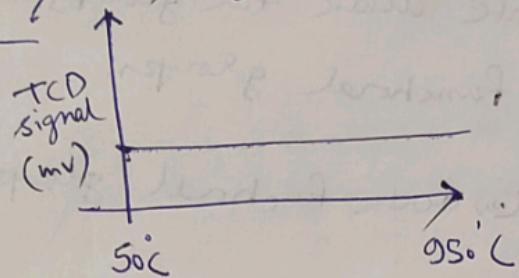
Case III → Instantaneous Intermediate acidic func group (only)



Case - IV : Weak acidic functional group.



case IV → No acidic functional group is present

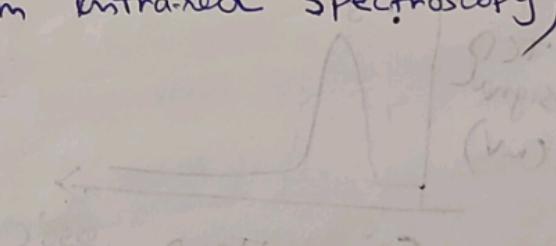
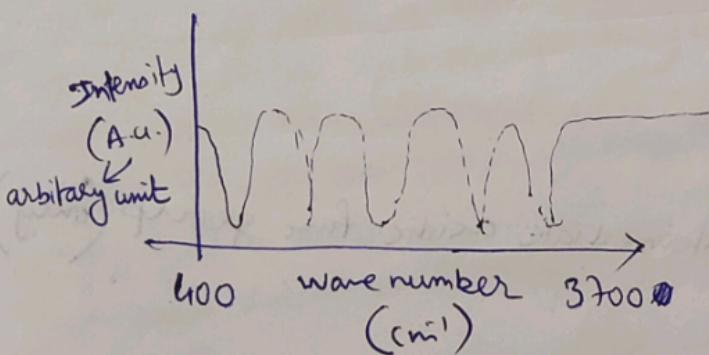


Difference b/w. Inconel and Stainless Steel

- Inconel is nickel-chromium alloy has high melting point than stainless.
- At high temp Inconel is preferred and low temp. stainless steel is preferred.

② Determination of functional groups.

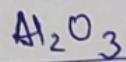
⇒ FTIR (Fourier Transform infrared Spectroscopy)



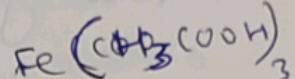
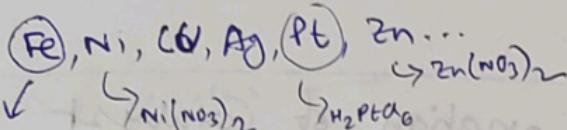
## Preparation of Catalyst (Heterogeneous)

$(\text{NH}_4\text{VO}_3)$

Support (99.99% Pure)



Next step  $\rightarrow$  Incorporation of active metal/metal oxide

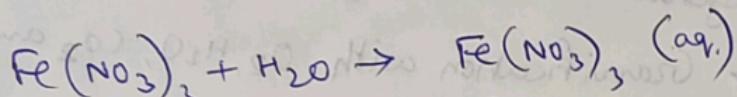


Precursors  
Precursor Salts :-  $\rightarrow \text{Fe}(\text{NO}_3)_3$ ,  $\rightarrow \text{FeSO}_4$ ,  $\rightarrow \text{Fe}$ -Acetate

req. to form catalyst

when  $\text{Al}_2\text{O}_3$  is mixed with say Fe, catalyst don't form.

Now,  $\text{Fe}_2\text{O}_3 / \text{Al}_2\text{O}_3 (\pm)$  = objective



Now,  
 $\text{Fe}(\text{NO}_3)_3$  [dissolve]  $\xrightarrow{\text{Al}_2\text{O}_3} \text{Parte will form.}$

Parte  $\xrightarrow[\text{atmosphere}]{\text{450°C, Air, 1 hour}}$  Muffle Furnace  $\xrightarrow[\text{(calcination operation)}]{\text{Fe}_2\text{O}_3 / \text{Al}_2\text{O}_3}$  reduction  $\xrightarrow[\text{H}_2, 550^\circ\text{C, 2 hr}]{\text{Fe} / \text{Al}_2\text{O}_3}$  Ball mixing  
 $\text{Fe}(\text{NO}_3)_3 \xrightarrow{\text{450°C}} \text{Fe}_2\text{O}_3 + \text{NO}_2 + \text{O}_2$  fine powder

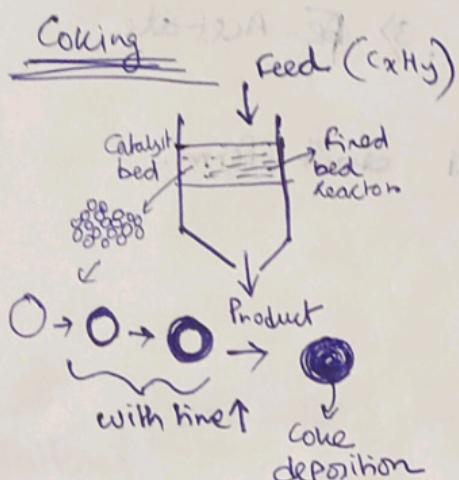
Reduction  $\xrightarrow{\text{Gas Phase (Reed; H}_2/\text{CO}_2/\text{H}_2\text{O}_2)}$   $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$  [Motto is to obtain  
 $\text{Fe}_2\text{O}_3 / \text{Al}_2\text{O}_3$ ]  
 liquid Phase  $[(\text{NH}_2\text{NH}_2)\cdot\text{H}_2\text{O} / \text{NaBH}_4 / \text{Citric acid}]$  (motto is same)  
 $\text{Fe}_2\text{O}_3 / \text{Al}_2\text{O}_3$   $\xrightarrow[\text{550°C, 2 hour}]{\text{H}_2}$   $\text{Fe} / \text{Al}_2\text{O}_3$   $\xrightarrow{\text{hydrazine mono-hydrate}}$

$\text{Fe}_2\text{O}_3 / \text{Al}_2\text{O}_3$   $\xrightarrow[\text{550°C, 2 hour}]{\text{H}_2}$   $\boxed{\text{Fe} / \text{Al}_2\text{O}_3}$   $\xrightarrow{\text{Ball milling}}$  fine Powder

if we use  $\text{Ag/SiO}_2$ , salt :-  $\text{AgNO}_3, \text{Ag}_2\text{SiO}_4$   
 $\text{Cu} \dots$ ,  $\text{Ag} : \text{Cu}(\text{NO}_3)_2,$

## # Deactivation of Catalyst —

- ↳ Coking
- ↳ Sintering → Narrowing of Pores
- ↳ Aggregation of active Particles.
- ↳ Poisoning.

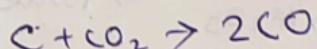
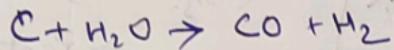


## Regeneration of Catalyst

The ability to reactivate a catalyst process depends on the reversibility of deactivation process.

### • Regeneration of catalyst Deactivated via Coking —

→ Granification with  $O_2$ ,  $H_2O$ ,  $CO_2$  and  $H_2$



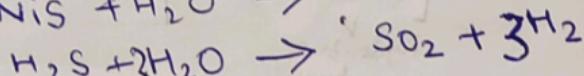
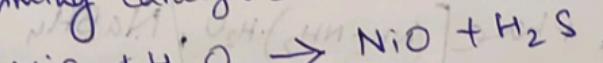
→ Promoters can also be added to increase rate of granification

→ Metal-catalyzed coke removal with  $H_2$  or  $H_2O$  can occur at temp as low as  $400^\circ C$  but more graphic or less reactive carbons on coke species in  $H_2$  or  $H_2O$  may req.  $700-900^\circ C$  temp.

### • Regeneration of Poisoned Catalyst

→ Treatment with  $O_2$  at low pressure and steam at  $700-900^\circ C$ .

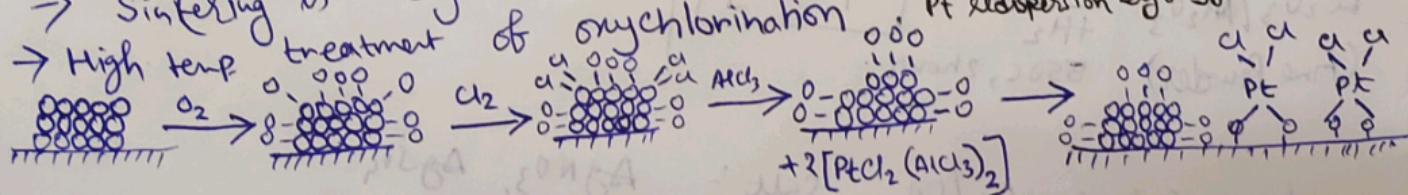
→ 80% removal of surface sulphur from Mg- and Ca-promoted Ni steam reforming catalysts occurs at  $700^\circ C$  in steam.



### • Redispersion of Sintered Catalyst:

→ Sintering is very hard to reverse

→ High temp treatment of oxychlorination



Prof. BB, 4th Sep

## ① Catalyst deactivation

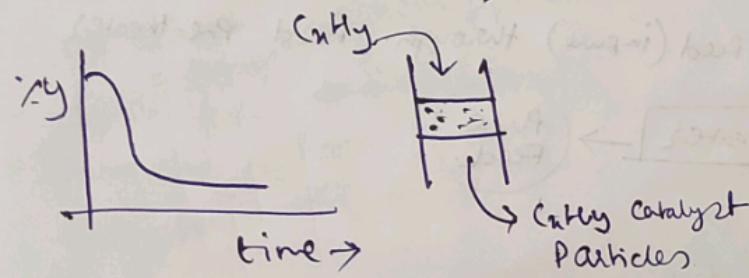
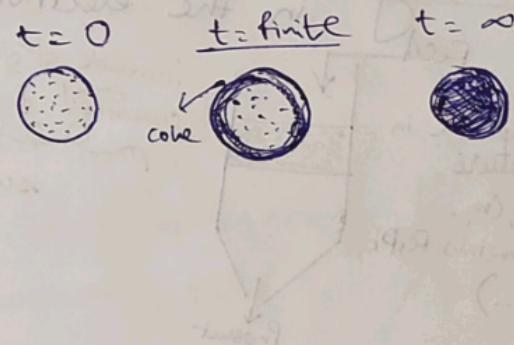
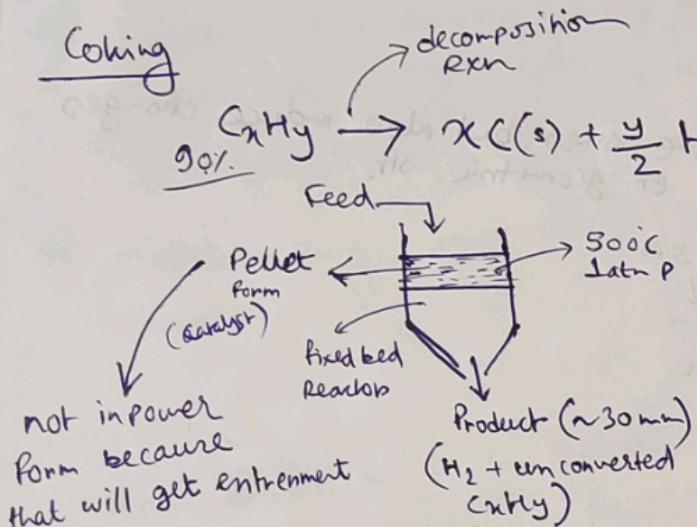
- 1) Coking
- 2) Sintering
- 3) Poisoning

Narrowing of Pores  
Aggregation of active metal/metal oxide particles.

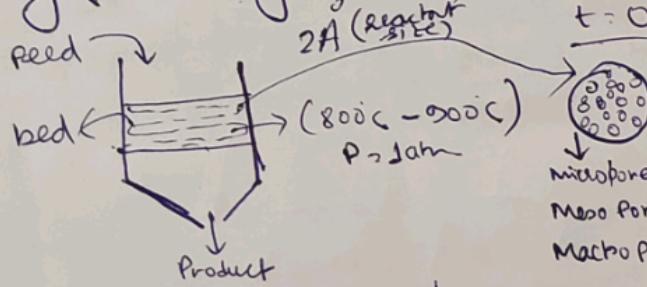
Coking: Com<sup>2+</sup> to reactions involving H<sub>2</sub>S.  
It results from a carbonaceous material (cone) deposited on the surface of a catalyst.  $\rightarrow$  (Pb, Hg, Zn, Sn, Cu, Fe)

Poisoning: Occurs when poisoning molecules are irreversibly chemisorbed to active sites, thereby reducing no. of sites for main reaction.

Sintering: It is the loss of catalytic activity due to loss of active surface area resulting from prolonged exposure to high gas phase temp. The active surface may be lost either by crystal agglomeration or closure of pores inside the catalyst pellet or narrowing of pores. A change in str. may also result.



## Sintering (Narrowing of Pores)



t = 0

micro pores ( $< 2$  nm)

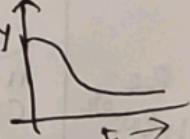
meso pores ( $2-50$  nm)

macro pores ( $> 50$  nm)

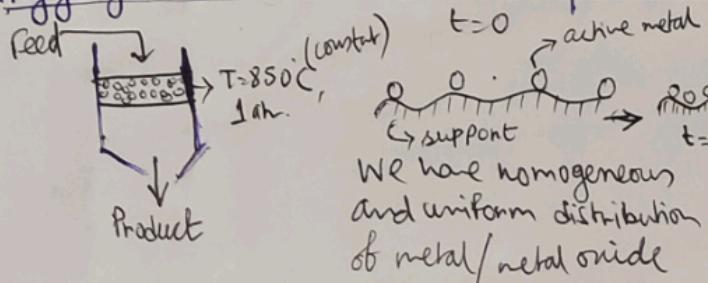
t = 24 h (T = 850°C, 1 atm)



Narrowing takes place

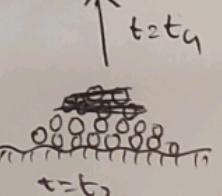
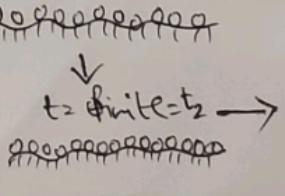
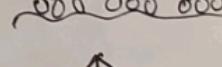
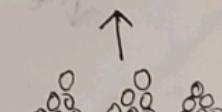
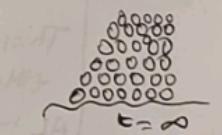


## Sintering (Aggregation of active metals/metal oxide)

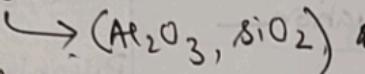


t = finite

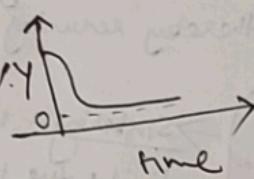
t = \infty



The distance between metal oxide are decreasing due to melting of oxide. The support is not melted as it is high thermal stability.

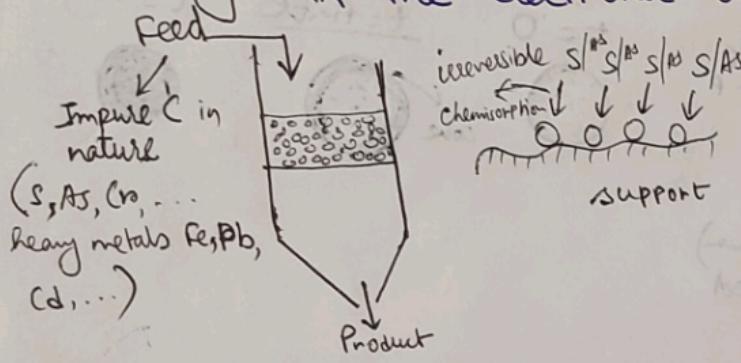


at final stage,

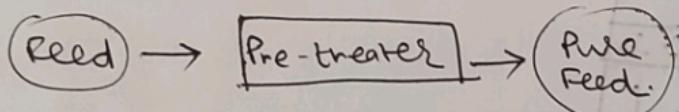


Productivity decrease because the feed is not able to get in touch with the active interval active metals, that part are not accessible.

# Poisoning: Not only block active sites, but also induce changes in the electronic or geometric str.

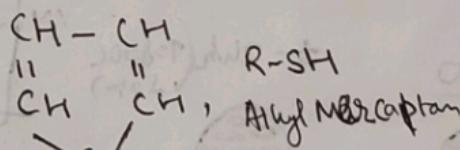


To avoid this, we can pass feed (impure) through feed pre-treater



Feed (rich in S-containing impurities)

Pre-treater unit



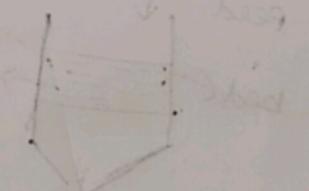
Thiophene

+ H<sub>2</sub>

At high pressure, 300-400°C

(acetone is primary) product 2

(acetone) 1  
acetone



(stainless steel liner to withstand)

compared with SW  
alumina rotatable  
steel liner (Vibrating)

Prof. B.B | 11th Sep

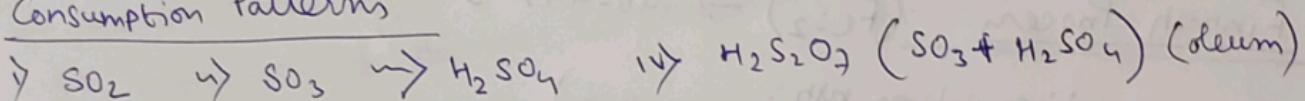
## S and $H_2SO_4$ Manufacturing

### Properties

- i) At. weight 32.07
- ii) Allotropes
  - Rhomboic (112.8°C)
  - Monoclinic sulphur (110°C)
- iii) B.P = 444.6°C
- iv) Solubility = Insoluble in water, soluble in liq.  $NH_3$  ( $NH_4OH$ ) and organic solvents.
- v) Availability →
  - Powder
  - Molten state
  - Rock → lumps.

foot  $2S + S_8 \xrightarrow{heat}$

### Consumption Patterns



### End Application

- Gunpowder ( $C + S + KNO_3$ )
- Inorganic chemical manufacturing industries.
- Organic chemical
- Paint Industry, Polymer industry, Rubber Industry, Paper-Pulp industry

### Production of Elemental Sulphur

- i) Frasch Process
- (USA)
- S-bearing salt domes + steam

→ Claus Process

(USA + India)

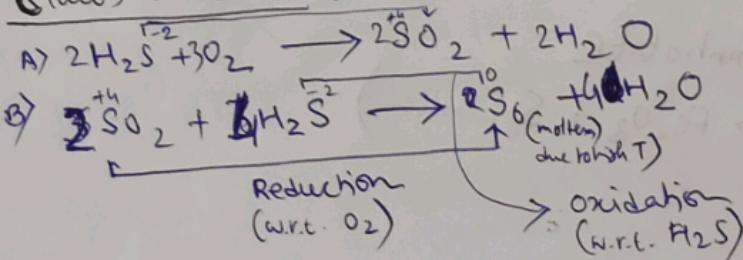
Oxidation and reduction of  $H_2S$

iii) Finnish Process.

(India)

(40-45% S)

### Claus Process



Coming

↓ (catalytic Activity)

Possibility 1 [less metal-support interaction]

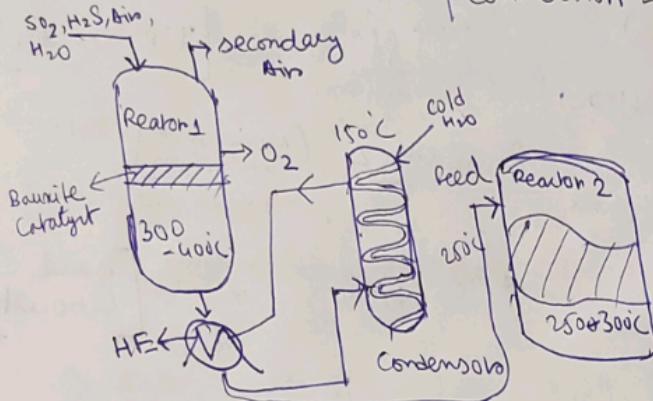
active metals → carbon nanotubes [Tip Growth]

Possibility 2 [More metal-Support interaction]

TIPS are all occupied → active metals [Bare Growth]

## Reactor 1

$T_2 = 300-400^\circ\text{C}$   
 $P_2 = 1\text{ atm}$   
 Catalyst = Bauxite ( $\text{Al}_2\text{O}_3$ )  
 Conversion = 70-80%



## Reaction - II

$T_2 = 250^\circ\text{C} - 300^\circ\text{C}$   
 $P = 1\text{ atm}$   
 Catalyst =  $\text{Al}_2\text{O}_3$   
 Conversion = 95-99%

⇒ Reason of 2 reactions

Main aim is to get more yield of sulphur.

In II-nd reactor we get 95% conversion. But if we use only that

then hotspot formation will take place and conversion will be less. So to avoid hotspot formation...

Frasch

Steaming

Drawbacks

Waste water

operat

o) ch

b) c

c)

d)

→ i

→ j

→ k

→ l

→ m

→ n

→ o

→ p

→ q

→ r

→ s

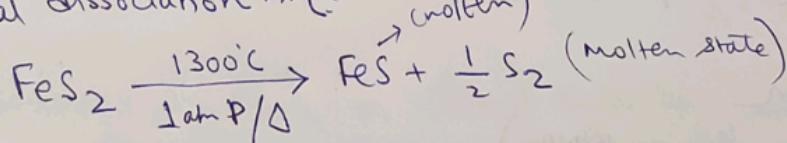
→ t

→ u

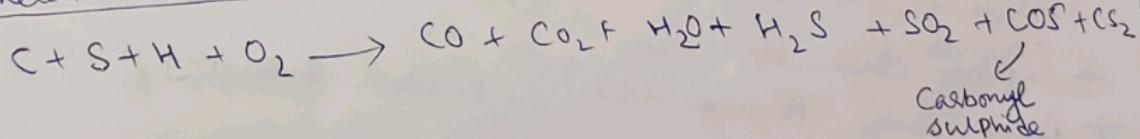
→ v

## Finnish Process ( $\text{FeS}_2$ ) $\rightarrow$ 40-45% S

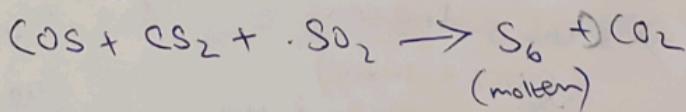
Thermal dissociation rxn:-



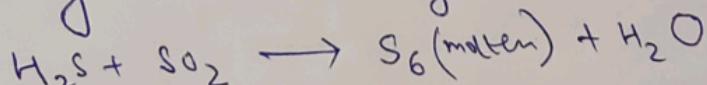
General Combustion Rxn



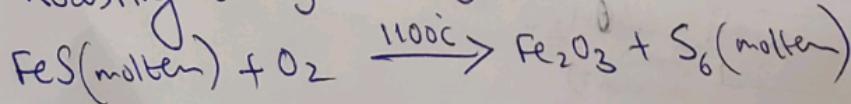
S-Recovery from Hot. Stage ( $600^\circ\text{C}$ , 1 atm,  $\text{Al}_2\text{O}_3$  Catalyst)



i) S-Recovery from cold storage



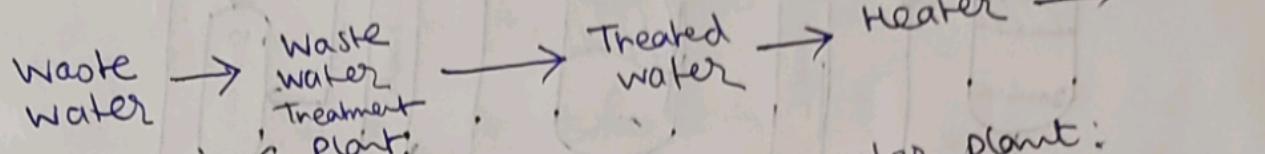
v) Roasting of Pyrotite Pyrrhotite



## ⑩ Frasch Process (USA) [high purity of S]

S bearing salt domes + steam → elemental sulphur

Drawback: sulfur formed corrodes surface of reactor



operation carried out in a waste water plant:

a) Chlorination (+ Cl<sub>2</sub>) → treated water / fresh water

b) Ozonation (+ O<sub>3</sub>) → fresh water

c) Advanced oxidation process (+ O<sub>2</sub>, at P ↑, 10 bar) T = 25°C

d) Fenton Rxn [FeSO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub>] → Fenton Reagent

→ major engineering problems:

i) corrosion of surface of reactor by elemental S.

ii)

→ Scrubbing Operation —

S contains acidic impurities. Scrubbing with monoethanol amine

Produces S (free of impurities)

