

Catalysis

Book: *Chemical Engineering Kinetics*, J. M. Smith, 3rd Edition, 2nd Edition (Chapter 7,8)
Elements of Chemical Reaction Engineering, H.S. Fogler, 4th Edition (Chapter 10)

- **Catalysts** play an important role in a **large number of industrial processes**
- Four of the largest sectors of our world economy (i.e. the **petroleum and power production, chemicals and polymer production, food and pharmaceutical industry and pollution control**) are largely **dependent on catalytic processes** - account for more than 10 trillion dollars of gross world product
- Over **90% of all chemicals** produced industrially involve the use of catalysts
- Some examples of processes that use catalysts are:
 - ✓ Production of inorganic chemicals (eg., ammonia, sulphuric acid)
 - ✓ Production of organic chemicals (eg., hydrogenation and polymerization)
 - ✓ Petroleum and petrochemical industry (eg., cracking, reforming and isomerization)
 - ✓ Production of synthetic fuels (eg., coal liquefaction and gasification)
 - ✓ Production of fine and speciality chemicals (eg., pharmaceuticals)
 - ✓ Control of pollutants (eg., industrial and automotive pollutant removal)
 - ✓ Energy conversion (eg., fuel cells)

Catalysts are substances that alters (accelerates or slows) the rate of a chemical reaction but remains unchanged after the catalytic cycle

- Depending on the phase of the catalyst and the reactants/products, the catalysts can be classified as **homogeneous** or **heterogeneous**
- **Homogeneous catalysis** refers to reactions where the *catalyst is in the same phase as at least one of the reactants*

Eg., Industrial Oxo process for production of iso-butylaldehyde

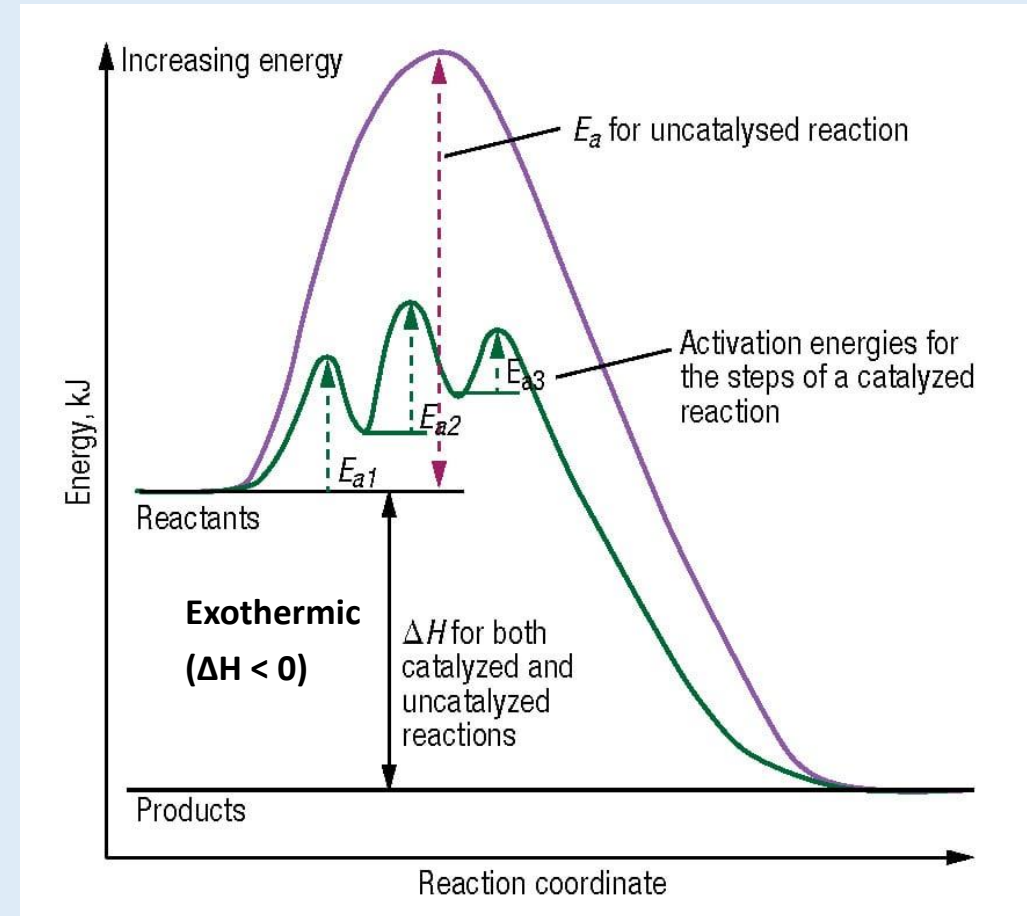
Reactants include propylene, carbon monoxide, hydrogen and a liquid phase cobalt complex (cobalt hydridocarbonyl) as the catalyst (temp - 140° to 180°C, pressure – 200 to 300 atm)

- **Heterogeneous catalysis** involves processes where there is *more than one phase – the catalyst is usually a solid phase and the reactants and products are in gaseous or liquid phase*

Eg., Haber's process for production of ammonia from hydrogen and nitrogen using iron oxide on alumina as solid catalyst

Characteristics of catalysis

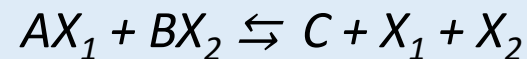
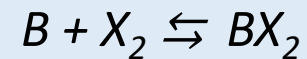
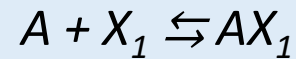
- A catalyst essentially **changes the mechanism** by which a particular reaction actually happens
- This **change in mechanism** or **the use of a different molecular path** helps to **change the rate** of the reaction
- The catalyst **reduces the potential energy barrier** (activation energy) over which the reaction must pass to form products (according to transition state theory)
- The alternate route chosen by the catalyst has a **lower free energy of activation** than the uncatalyzed process
- In the Fig., the three peaks shown for the catalyzed reaction indicate the three intermediate steps of the reaction



Activation energy of a catalytic step is less than that of the non-catalytic reaction

- Although a catalyst remains unchanged at the end of the catalytic reaction, the **catalytic material actively participates** during the course of the reaction
- The catalytic reaction occurs on the surface of the catalyst at *special sites* called the **active sites**
- Phenomenon of catalysis can be explained by the **formation of a complex between the reactant and an active catalyst centre**

The reaction $A + B \rightleftharpoons C$ is catalyzed by two active sites X_1 and X_2 which form complexes with A and B and are regenerated after formation of C



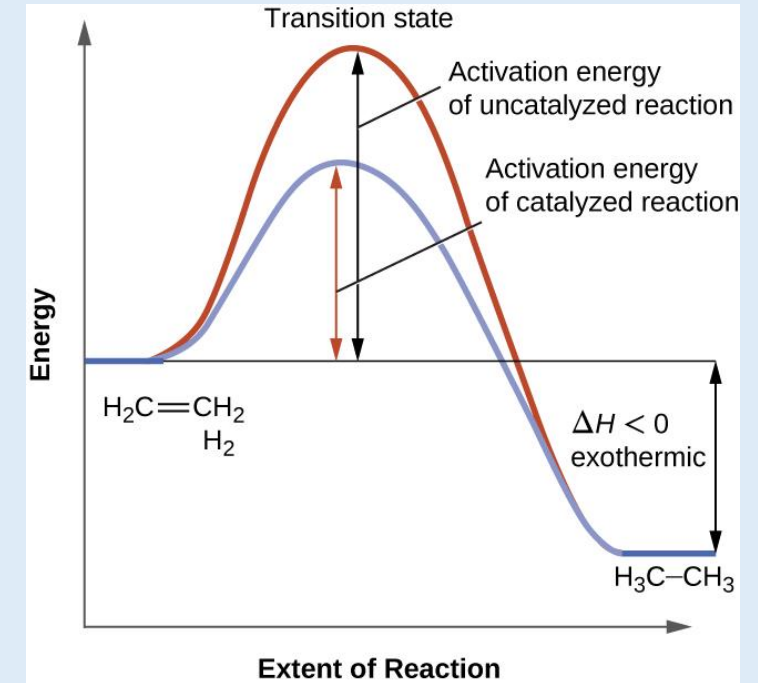
The regenerated sites X_1 and X_2 can again be used for reaction

- The **catalytic ability of the active sites do not remain constant** forever, active centres becomes deactivated over a period of time

In the reaction cycle, the active centres (sites) of catalysis first combine with at least one reactant and are then reproduced with the appearance of the product

- A catalyst helps to reduce the activation energy required to form the products
- **ΔH for the reaction** (characterised by the difference in the energy between the products and reactants) is **not affected by the catalyst**
- A catalyst changes only the rate of a reaction and **not the equilibrium**, it **helps in achieving the equilibrium faster**
- For a reversible reaction, **catalyst alters the rate of both the forward** as well as **backward reaction**

Eg., oxidation of SO_2 by O_2 carried out over three different catalysts – platinum, ferric oxide and vanadium penta-oxide is seen to have the same equilibrium composition



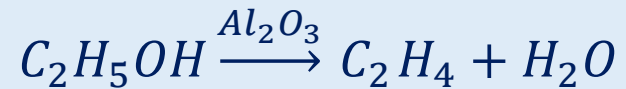
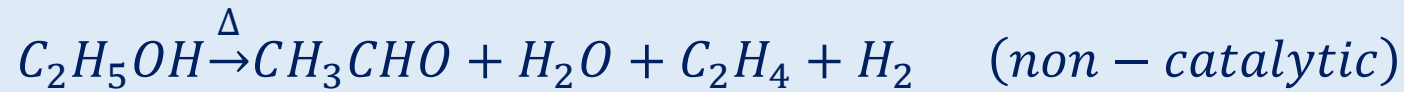
Equilibrium conversion is not altered by catalysis, it is governed by thermodynamics alone

- **Small amount** of catalyst can cause **conversion of a large amount** of reactant
- For homogeneous catalyzed reactions, in most cases the rate of the reaction is directly proportional to the catalyst concentration
- For surface catalytic reactions, the rate is often proportional to the active sites on the surface or the surface area

Small quantities of catalytic sites are required to produce large amounts of product

- Catalysts use an **alternate path to form products** and has a profound **effect on yield and selectivity**
- Use of an appropriate catalyst helps in **enhancing** the rate of the **desirable reaction** (to obtain high selectivity)

Eg. Decomposition of ethanol with and without catalysts yield different products

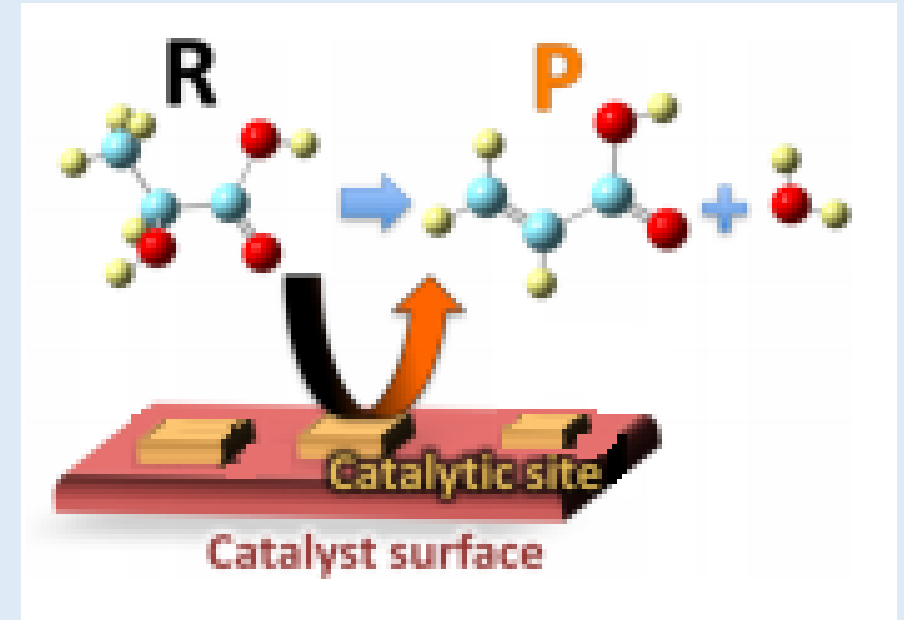


- High selectivity catalyst actually has a strong implication in terms of the overall economy of producing that particular desired product

Catalysts radically alter the selectivity of a reaction

Solid catalysts

- Heterogeneous catalytic reactions occur at the **fluid-solid interface**
- Reaction is carried out on **certain active sites** on the solid surface and not the entire surface
- **An active site** is a point on the catalyst surface that can form strong chemical bonds with an adsorbed atom or molecule
- **Large interfacial area** is beneficial for achieving **significant rates**
- **Large interfacial area** (high probability of presence of active sites) are provided by **porous material**; surface area of catalysts range from 5-10 m²/g – 1000 m²/g
- **Activity** of a catalyst is proportional to the number of active sites and is often quantified by **Turnover Frequency (TOF)** – *TOF is the number of molecules reacting per active site per second under experimental conditions*
- **Dispersion** of a catalyst is the fraction of the metal atoms deposited on the surface



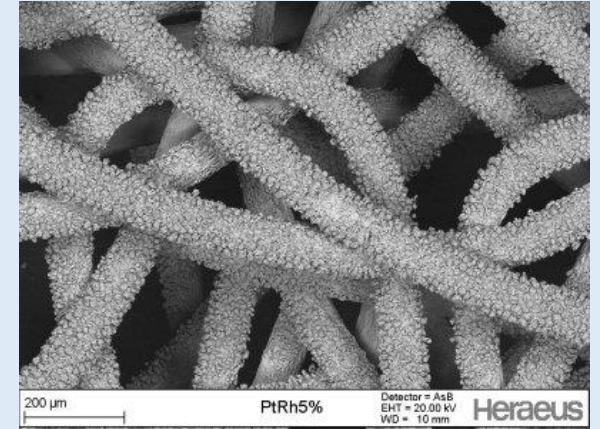
Types of catalysts

Unsupported (bulk) catalysts

- *entire catalyst* consists of catalytically active material
- typically *very active* and *does not require very high surface area* (Pt wire gauze used for ammonia oxidation) or intrinsically have high surface area ($\gamma\text{-Al}_2\text{O}_3$ for isomerization)



Pt wire gauze



Scanning electron micrograph of Pt wire gauze

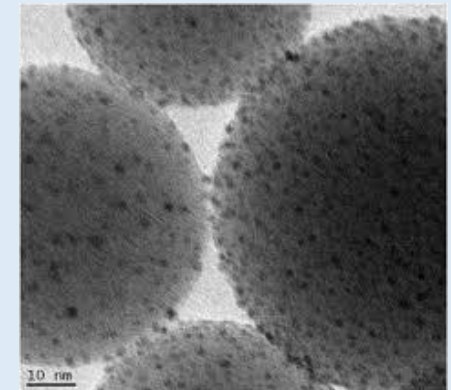
<http://www.chemgapedia.de/>

Supported catalysts

- *catalytically active material is dispersed over a high surface area support* (Pt on Al_2O_3 used in petroleum reforming, V_2O_5 on SiO_2 used for SO_2 oxidation)
- better the dispersion of the active material on support, more effective is the catalyst



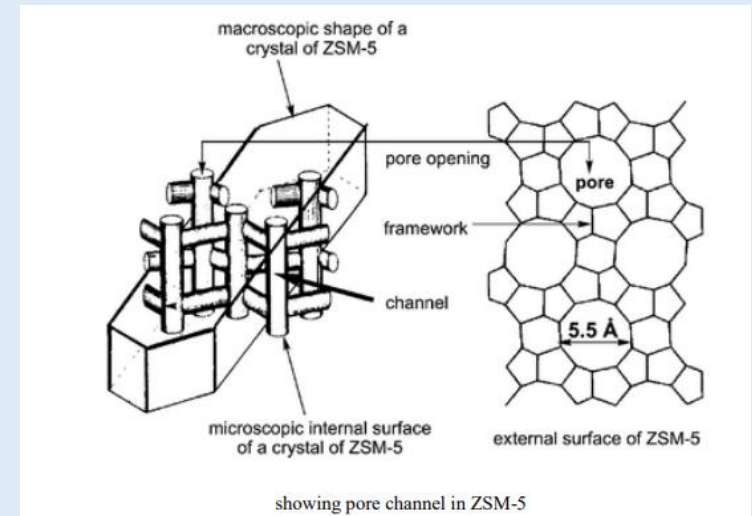
Pt on Al_2O_3 spherical pellets



TEM micrograph of Pt/ Al_2O_3 , Pt particles indicated by the black dots

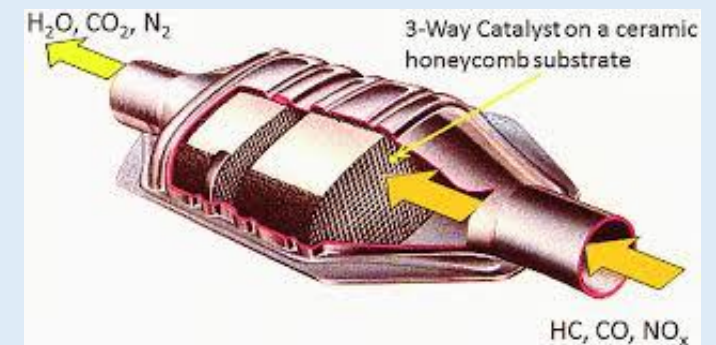
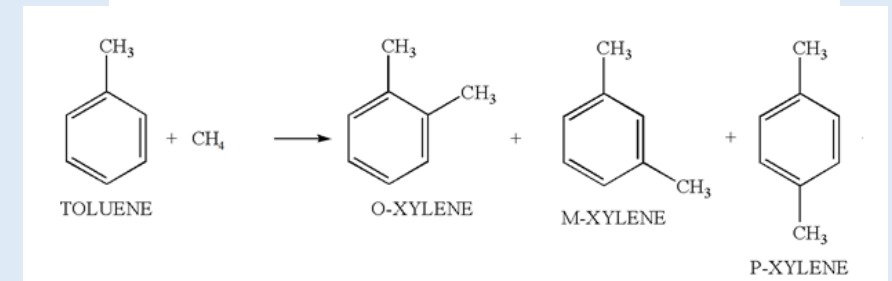
Molecular sieves

- These catalysts have extremely narrow and regular pores (5-15 Å)
- Act as *shape selective catalysts* (facilitates good selectivity for a desired product)
- The *regular narrow structure of the pores* allows some molecules to enter, excludes others and causes some to break down
- Example: zeolite (aluminosilicates) catalyst



Monolithic catalysts

- These are *structured catalysts*
- Have the advantage of low pressure drop, uniform distribution of catalyst over large surface area, efficient mass transfer, high mechanical strength, ease of product separation
- May have a honeycomb structure (catalytic converters in automobiles) or can be in the form of needles (Ag needles for methanol to formaldehyde conversion) or wire gauze



Molecular sieves

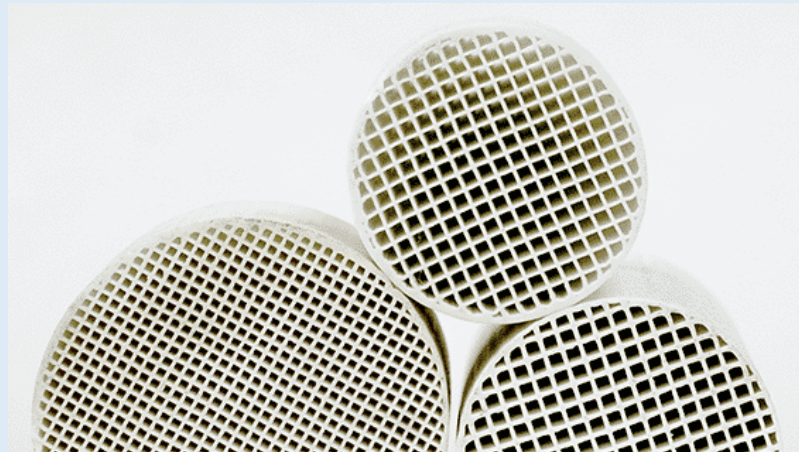


ZSM5 powder

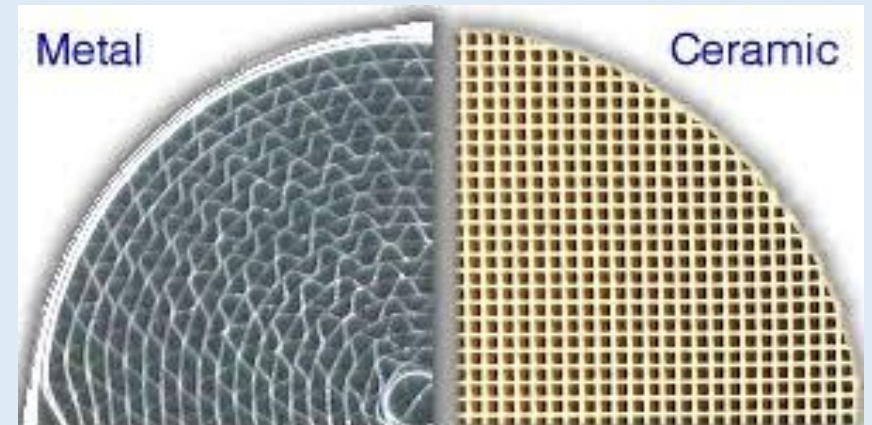


ZSM5 pellet

Monolithic catalysts



Ceramic monoliths



Metal and Ceramic monoliths

Choosing the active catalytic species

- When deciding on an active catalytic species for a particular reaction, it is necessary to **list which of the bonds of the reactant needs to be ruptured, and which are not desirable to activate**
- Metallic Fe is a good catalytic species for **synthesizing NH₃ from N₂ and H₂** - both N-N and H-H bond needs to be ruptured
Ru, Mo are also good catalysts but more expensive than **Fe**
- For **CH₃OH synthesis from CO and H₂**, it is necessary to activate CO and H-H but not the bond between C and O – activation of C-O bond would lead to formation of CH₄, C, paraffins, waxes etc (all undesirable) instead of CH₃OH

Choice from species for H activation, CO activation but not C

Most widely used catalyst is mixture of Cu, ZnO

Selection of catalytic species

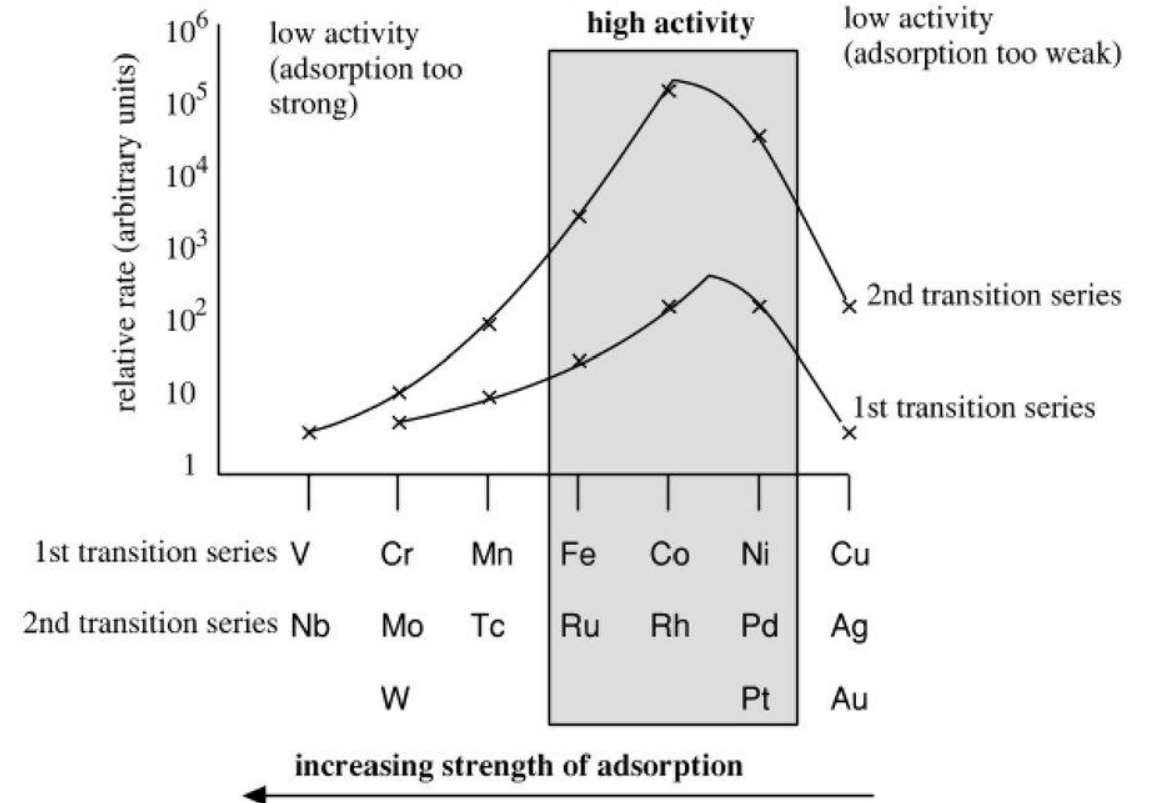
| ACTIVATION REQUIRED | STATE OF CATALYST | HIGH ACTIVITY | MEDIUM ACTIVITY |
|-----------------------------------|------------------------|---|--|
| H - | METAL, OXIDE, SULPHIDE | Pd, Pt, Rh, Ru, Ir | Mn, Fe, Ni, Cu, W, Ag, Cr, Co, Zn, V, Mo |
| O = | METAL OR OXIDE | Pt, Pd, Mn, Co, Cu | Ag, Ni, Fe, V, Mo, Sb, Cr, Ti |
| C ≡ | METAL | Fe, Ru, Os, Rh | Ni, Co |
| N ≡ | METAL | Fe, Ru, Os, Mo | W, Mn, U |
| S = | SULPHIDE | Mo, W | Co, Ni, Cu, Fe, Sn, Zn, V |
| C | CARBONATE | K, Na | Ca |
| Cl - | CHLORIDE | Cu, Zn, Hg, Ag | |
| H ₂ O, OH ⁻ | OXIDE OR HYDROXIDE | W, P, V, Co, Th, Mg | B, Al, Ti, Hg, Zn, Si, Al |
| H ⁺ | OXIDE OR HALIDE | (Si, Al, P, Cr, W) OXIDES | (Al, Sn, Zn, Zr, B) HALIDES |
| HCl | OXIDE OR CHLORIDE | Si, Al, Al | |
| C=C=C | METAL OR OXIDE | Pd, Pt, Rh, Ru | Co, Ni, Fe, Ir, W, Mo, Cr, Cu |
| C=C | SALTS | Hg, Cu, Ag | Zn |
| CO | METAL OR OXIDE | Pt, Cu, Pd, Ir | Zn, Co, Fe, Mn, Ag |
| SO ₂ | METAL OR OXIDE | Pt, V | Fe, Al |
| NONE | OXIDE | Al, Mg, MgAl, Mg Si, Ca Al ₂ | |

Bond activations associated with different species

Ref: S.P.S. Andrew, Chem Eng Sci, 36(9), 1981, 1431-1445

- **Transition metals and their compounds** are usually good catalysts
- They have **partially filled d-orbitals** which can be used to make *temporary bonds by accepting or giving electrons*
- They have the *ability to be in a variety of oxidation states* and to interchange between the oxidation states
- The figure shows the *relative reaction rate versus strength of adsorption for different transition metals*
- Very strong adsorption (eg., W) or very weak adsorption (eg., Ag) lead to low activity – reactants are either so strongly adsorbed that they cannot move and products not desorbed or reactants are not adsorbed enough
- Strength of adsorption seems to be just adequate for Fe, Co, Ni, Pd, Pt etc (grey box)

Heterogeneous Catalysts

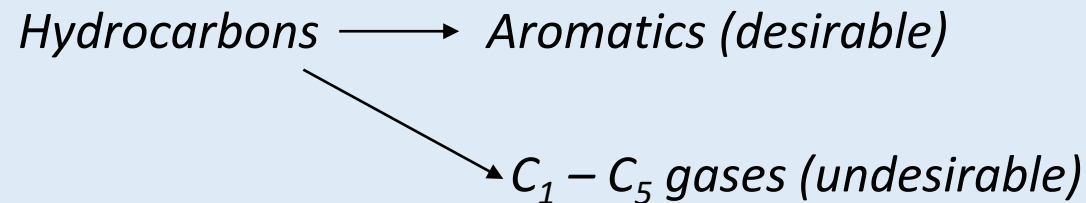


<https://nptel.ac.in/courses/103/102/103102012/>

Methods to enhance catalyst selectivity

- **To poison undesirable activity**

Catalyst surface modified by *chemisorbing an inert poison* which does not react with reactant or product

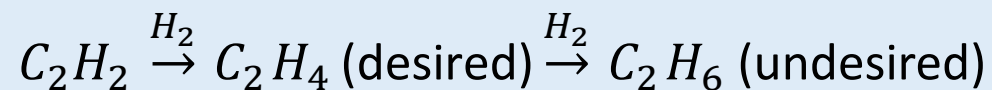


H₂S (a S compound) added to reduce activity so that C₁-C₅ gases are not formed

- **To inhibit consecutive reaction**

An *inert adsorption competitor* is added to prevent further reaction

For hydrogenation of CH₃CH to CH₂=CH₂ over Pd catalyst, small amount of added CO prevents the CH₂=CH₂ from getting further adsorbed on the catalyst to form CH₃-CH₃

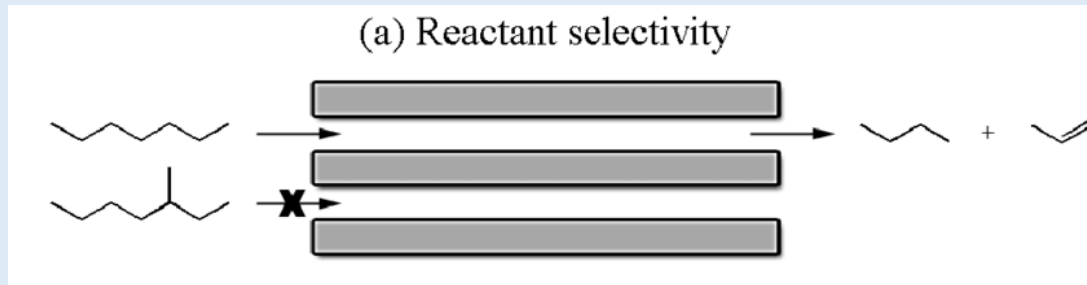


- **To limit molecular size**

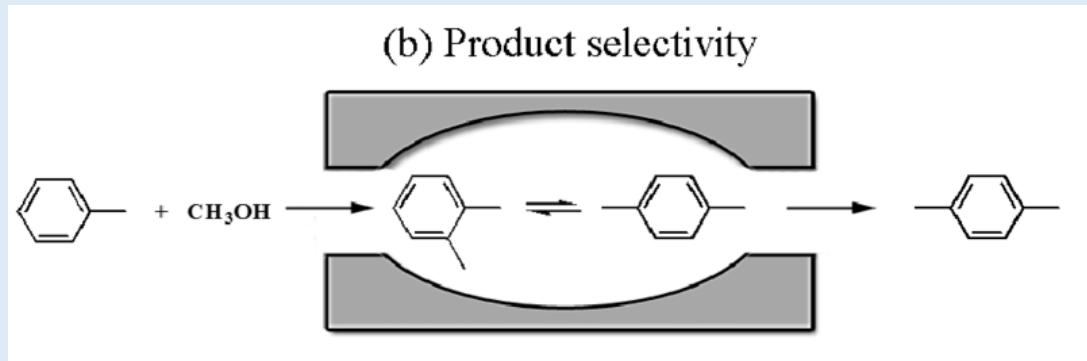
A zeolite catalyst which has a regular, cage like structure can be used

Pore size of the catalyst will prevent large molecules from entering and also prevent large product molecules from being formed

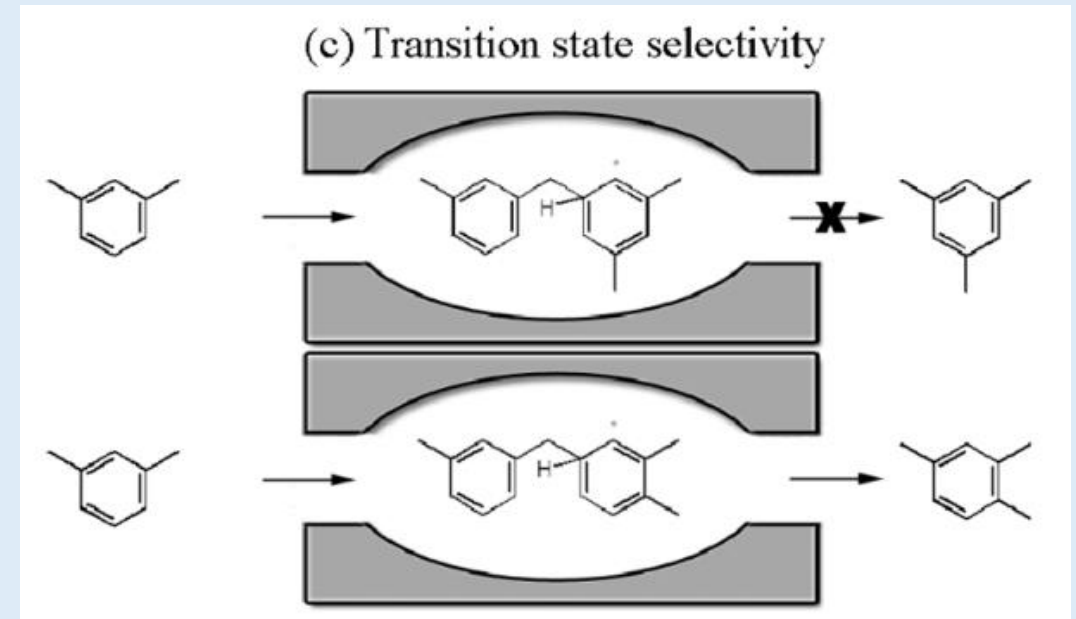
Pore sizes also *control the type of transition state* that may be formed



(a) Reactant selectivity: cleavage of linear hydrocarbons,



(b) Product selectivity: methylation of toluene,



(c) Transition state selectivity: disproportionation of m-xylene.

Poisons for the catalyst

- **Surface active metals or ions**

Steam reforming of CH_4 to form CO is carried out in the presence of a Ni catalyst -

Low concentrations of Cu in the Ni may deactivate the catalyst as Cu is more surface active than Ni (Cu has lower surface tension) and will cover the Ni sites

Low amounts of Ca in Co_3O_4 catalyst for ammonia oxidation diffuses to the surface and deactivates the catalyst

- **High molecular weight product producer**

Species which accelerates the formation of high molecular weight 'polymer' or 'coke' acts as a poison

Coke deposits on the surface and deactivates the catalyst, Eg., Fe in $SiO_2-Al_2O_3$ cracking catalyst

- **Strong chemisorber**

A species which attaches to an active site permanently renders the active site useless for reaction,

Sulphur for Ni, Pt catalyst and NH_3 for $SiO_2-Al_2O_3$ catalyst are examples

- **Sintering accelerator**

During the reaction, due to high temperature, crystallites on the catalyst migrate from their position and tend to form clusters

Causes a loss in surface area and activity - presence of H_2O for Al_2O_3 and Cl_2 for Cu catalyst enhance sintering

Few related terms

Promoter

- ✓ This is a *substance that is added to a solid catalyst to improve its catalytic activity or selectivity*
- ✓ Promoters themselves may have very little or no catalytic activity
- ✓ They *interact with the active component of the catalyst and alter their chemical effect by causing changes in the electronic or crystal structure* of the active solid compound
- ✓ Mo is used as a promoter with Fe catalyst for NH_3 synthesis

Stabilizer

- ✓ These are substances *added to prevent the sintering and agglomeration of catalyst particles*
- ✓ Al_2O_3 on Fe-based NH_3 catalyst

Binder

- ✓ These are added when powder catalysts are converted into pellets
- ✓ They provide the catalyst *necessary mechanical strength and/or resistance towards attrition loss*
- ✓ Silica and alumina or natural clay, such as kaolin, kaolinite etc can be used as binders