

## Lecture 36

### Zeolites

#### Composition and structures

Zeolites are crystalline aluminosilicates with pores of molecular dimensions. The general formula for a **zeolite** is  $M_{x/n}[(AlO_2)_x(SiO_2)_y].mH_2O$ . M is the metal or hydrogen cation of valency 'n' occupying the exchangeable cationic sites on zeolite framework.  $AlO_2$  and  $SiO_2$  are fundamental units sharing oxygen ions to form tetrahedral  $AlO_4$  and  $SiO_4$  building blocks for zeolite unit cell. Since silicon ion has +4 and Aluminium has +3 charges there is an overall negative charge on the aluminosilicate framework. The cationic charge of the metal or hydrogen **ion** balances the negative charge on the aluminosilicate framework.

Aluminosilicates are formed by polymerization of  $SiO_4$  and  $AlO_4$  tetrahedra to form sheet like polyhedral. The polyhedra forms cubes, hexagonal prisms and truncated octahedral. These 3D tertiary building blocks in turn are arranged regularly to form a superstructure inside which pores and supercage exists. Each supercage is characterized by a window size aperture which can block entry of sufficiently large molecules. This is known as sieve effect. The zeolite structures have pores oriented in one, two or three directions leading to 1D, 2D, 3D structures. Structures of zeolite X and A is shown in Fig 1.

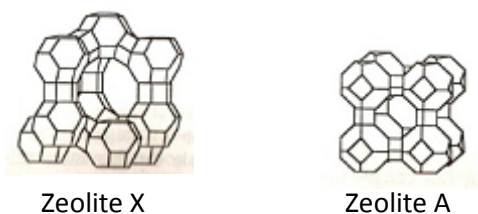


Fig 1. Schematic diagram of zeolites structures

Zeolites are classified based on their pore diameter and ring size. Among aluminosilicate zeolites 3A, 4A, 5A and erionite containing 8 number of rings have pore diameters in the range of 3-5 Å. ZSM 5 and mordenite with 10 and 8 rings respectively have pore

diameters in range of 3-5 Å. On the other hand, faujasite X and Y have 12 rings with larger pore diameter of 7 - 8 Å. Aluminophosphates (ALPOs) have significantly extended range of pore sizes. ALPOs containing 12 rings have pore diameter of 10 Å while 18 ring ALPOs have pore diameter of 10-15 Å.

**Table 1. Compositions of common zeolites per unit cell**

<b>Zeolite type</b>	<b>Na</b>	<b>AlO<sub>2</sub></b>	<b>SiO<sub>2</sub></b>	<b>H<sub>2</sub>O</b>
Zeolite A	12	12	12	27
Zeolite X	86	86	106	264
Zeolite Y	56	56	136	264
ZSM-5	9	9	87	16
Mordenite	8	8	40	24

### **Preparation of zeolites**

Zeolites are synthesized by crystallization from reactive forms of silicon, aluminum, sodium, sodium hydroxide and organic template at 90-180 °C and 1-10 atm pressure. The pH is maintained higher than 10. Seed crystals are added to the reactor to initiate the crystallization process. Typical crystallization time varies in the range from 16-36 h. Organic template is added to facilitate formation of pores and supercages. Typically organic template is an organic amine or alkyl ammonium compound. Crystallization of the gels proceeds around the template molecular mold producing the porous network. The synthesis of various zeolites is achieved by varying the synthesis conditions such as temperature, pH, crystallization time, order of mixing and amount of Si, Al, Na, and H<sub>2</sub>O. Laboratory preparation of NaX Zeolite and ZSM-5 zeolite is discussed below.

**Preparation of ZSM-5 zeolite [1]**

Aluminum nitrate and colloidal silica are added to a stirred mixture of tetrapropyl ammonium bromide and sodium hydroxide solution to give a hydrogel. Then, the hydrogel was transferred to a stainless-steel autoclave with a Teflon lining and placed in an oven for appropriate periods. After the completion of crystallization under autogeneous pressure, the autoclave is cooled down, samples are washed and dried at 120 °C for 24 h. Finally, the sample is calcined at 500 °C for 16 h to remove the organic base occluded in the zeolite framework, protonated in hydrochloric acid solution at room temperature for 24 h, and then again dried at 393 K.

**Preparation of NaX Zeolite [ 2]**

The sodium silicate and sodium aluminate are prepared separately. The silica gel and aluminum isopropoxide is used as starting materials for silicon and aluminum respectively. The sodium silicate is prepared by adding silica gel, sodium hydroxide, and deionized water to a plastic beaker stirred until the solids are completely dissolved. The sodium aluminate solution is prepared simultaneously by adding aluminum isopropoxide, sodium hydroxide, and deionized water. The mixture is stirred below 80 °C until the solids are dissolved to form a clear gel and the mixture is cooled to room temperature. Then the aluminate solution is added to the silicate solution with additional amount of water. The final mixture is stirred until homogenous and then placed in an oven for 24h at 90 °C. After 24 h, the mixture is cooled to room temperature giving white zeolite crystals. The crystals are washed thoroughly with water, filtered and air-dried.

**Properties of zeolites****a. High surface area and ordered pore structure**

High surface area and ordered pore structure of zeolites result in their unique adsorption properties. Zeolites are characterized by large surface area because of its highly porous nature. The surface area of zeolites is in the range of 600-800 m<sup>2</sup>/g. As a result of high surface area zeolites can adsorb large quantities of adsorbate depending on adsorbate size, aperture size, temperature and surface acidity of zeolites.

Zeolites have aperture or pore diameter of the order of molecular dimension therefore molecules having diameter of the same order or larger than pore diameter or aperture are excluded from entering the pores or super cages. Since larger molecules are excluded, preferential adsorption and reaction can be done using zeolites. For examples separation of  $O_2$  and  $N_2$  in air can be done using and 13 X-NaX zeolites.

**a. Acidity :**

The OH bridging a framework of silicon to a framework of aluminum acts as the Bronsted acid site. Coordinately unsaturated Al sites give rise to Lewis acidity. Acidity in zeolites increases with decreasing Si: Al ratios because acid sites are associated with Al ions. Bronsted and Lewis acid sites play important roles in various catalytic reactions involving hydrocarbons. Zeolites are used in catalytic cracking reaction in petroleum industry.

**b. Thermal stability :**

Most of the zeolites are stable upto 400 °C. Stability increases with increasing silica content. Introduction of rare earth cations in zeolites result in stability upto 800 °C

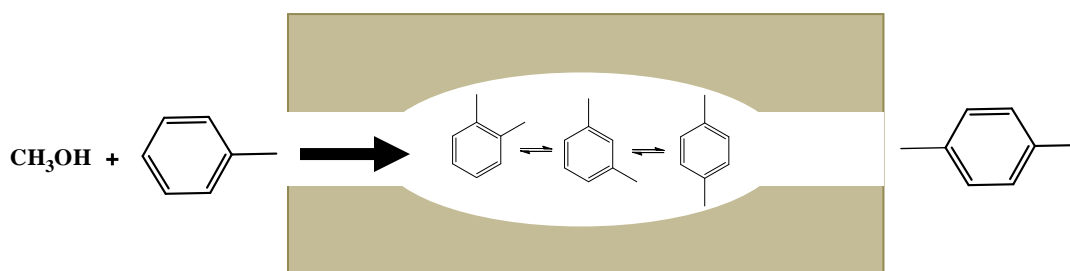
**c. Shape selectivity**

Unique pore structure of zeolites results in its high shape selective properties. Shape selectivity results due to:

- geometric restrictions on the access of reactants to the zeolite framework
  - geometric restrictions on diffusion of reactants in or diffusion of products out from catalysts
- i. Reactant selectivity : Selective admission of reactants to zeolite pores due to pore size restrictions is known as reactant selectivity. For example in case of cracking reactions, n-heptane undergoes preferential cracking (relative rate 1) over dimethylhexane (relative rate 0.09). The dimethylhexane, due to presence of branched carbons, is unable to enter the zeolite pores.



- ii. **Product selectivity :** When there is possibility of formation of multiple products , selective formation of product can occur due to restriction on size or diffusion rates of the larger molecule. For examples when alkylation of methylbenzene is carried out over pentasil zeolites all isomers p-xylene, m-xylene, and o-xylene are probable products. However, due to pore diameter restrictions in pentasil zeolites there is preferential production of p-xylene over ortho and meta forms as shown in the figure below.



- iii. **Molecular traffic control :** This concept involves preferential diffusion of reactants through one channel and diffusion of products out of another interconnecting channel of a zeolite. Counter diffusion is minimized and product selectivity is maximized by this process.

## Characterization of zeolites

The physicochemical properties of zeolites are studied by various characterization techniques such as XRD, FTIR, SEM etc. Fig. 2 gives the XRD profile of zeolites Y. The presence of sharp peaks indicates high crystalline nature of zeolites. The peaks correspond to different crystal planes in zeolites as shown in Fig 2. The Fig. 3 shows the SEM image of zeolite Y. The surface acidity of zeolites can be measured using pyridine probe in FTIR analysis or  $\text{NH}_3$ -TPD.

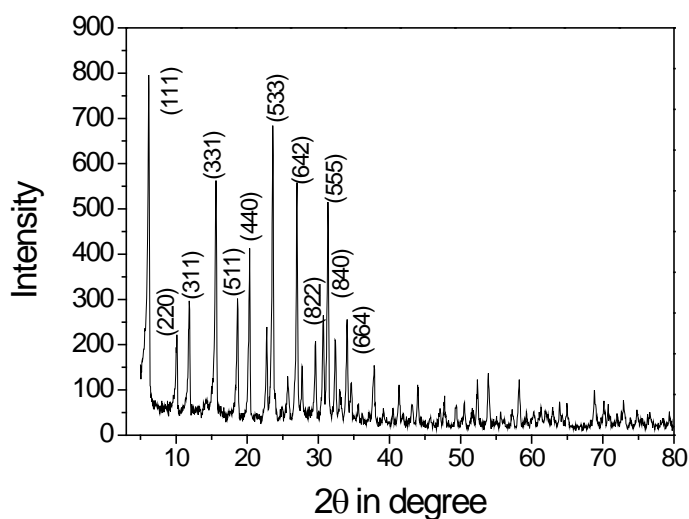


Fig 2. Typical XRD profile of Zeolite Y

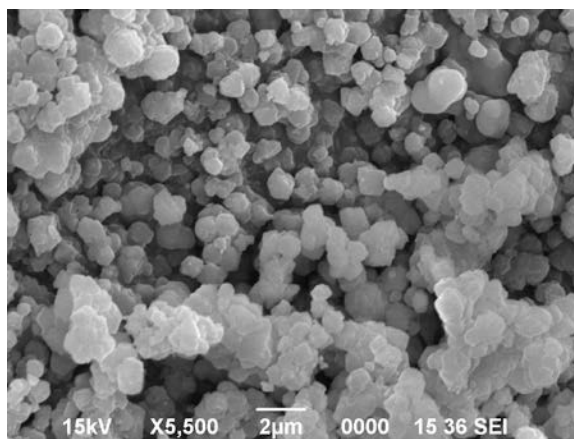


Fig.3. SEM image of zeolite Y.

## Applications of zeolites

The principal applications of zeolites are discussed below.

### i. Catalysts and catalyst supports

Acidity and shape –selective properties of zeolites play major roles in their use as catalysts to produce premium quality fuels and chemicals. Zeolites because of their acidity find applications in catalytic cracking, isomerization, alkylation and aromatization reactions. Fluidized catalytic cracking is the largest and oldest application of zeolite catalysts. Medium pore zeolites are being widely used in conversion of light hydrocarbons to monocyclic aromatics, because of their ability to selectively perform these reactions, while minimizing coke formation. For same reactions, when small pore zeolites are used, no aromatics are produced and severe operating conditions are required, whereas large pore zeolites produce heavy aromatics and deactivate rapidly. The major advantage of large pore molecular sieves, developed recently, is their ability to crack larger molecules, such as present in heavy petroleum residue, more efficiently. Major commercial catalytic processes using zeolites are summarized in Table 1.

**Table 1. Commercial catalytic processes using zeolite catalysts**

<b>Zeolites</b>	<b>Process</b>	<b>Products</b>
Faujasite	Catalytic cracking	Gasoline, fuel oil
Faujasite	Hydrocracking	Kerosene, jet fuel, benzene, toluene, xylene
Mordenite	Hydroisomerization	i-hexane, heptane
ZSM -5	Benzene alkylation	Styrene
ZSM -5	Xylene isomerization	p-xylene

In addition to the well established commercial processes some other new applications of zeolites are being developed. Conversion of n-hexane and n-heptane to benzene and toluene is carried out on a PtBa/Zeolite L catalyst while, isomerization of  $C_5/C_6$  is done with Pt/mordenite /alumina catalyst. For ZSM-5 catalysts various applications are developed. For example, alkylation of benzene and toluene to form high octane alkyl aromatics, methanol to gasoline, methanol

to alkene, toluene disproportionation to p-xylene, or selective catalytic reduction of NO has been reported with ZSM-5 or modified ZSM-5 catalysts.

ii. Selective adsorbents and drying agents

Zeolites have unique ability to adsorb water while rejecting larger molecules. For many applications they are the best available drying agents. Used in drying air, natural gas, organic solvents and refrigerants.

iii. Separation and purification of gasses and liquids

Zeolites are used in purification of gases and hydrocarbon liquids. The 5A (CaA) and 13X(NaX) zeolites have been the most commonly used sorbents for air separation. The typical commercial 5A used for air separation is made by exchanging ~70% of the  $\text{Na}^+$  in NaA by  $\text{Ca}^{2+}$  ions. The nitrogen is preferentially adsorbed on the zeolite.

iv. Various types of zeolites such as Zeolites A,X, ZSM-5, mordenite etc. are used for removing  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{CO}_2$  and other impurities from gas stream. In gas cleaning, zeolites are normally used for the removal of  $\text{H}_2\text{O}$ ,  $\text{SO}_2$  and  $\text{CO}_2$  from sour natural gas stream. Zeolite 4A are used for removal of  $\text{CO}_2$  from submarines and spacecraft. The CaA (Ca ion exchanged zeolites A) is used to adsorb  $\text{H}_2\text{S}$  from sour gas. They are also used for selective removal of  $\text{NH}_3$  produced during gasification of coal and for removal of  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{CO}_2$  from air. Separation of close boiling point mixtures of alkylphenols, such as mixture of p-cresol (201.8)/2,6-xylenol (203 °C) or m-cresol (202.8 °C)/2,6-xylenol has been attempted using Na-X zeolites[3]. Effect of the cation on the selectivity has also been investigated. The Na-X zeolite adsorbs p-cresol and m-cresol selectively from their mixtures with 2,6-xylenol, while Ca-X and Ba-X zeolites preferentially adsorb 2,6-xylenol. The selectivity seems to be decided by the diffusion in the zeolite framework.

v. Water and waste water treatment :

In water and waste water treatment zeolites are used for various purposes, mainly for water softening, ammonia removal and heavy metal removal. Zeolite is used for exchange of hard ions [ $\text{Ca}^{+2}$ ] with soft ions [ $\text{Na}^+$ ,  $\text{H}^+$ ] for softening water in a



broad range of pH values. It is one of the oldest applications. This is particularly important in detergent industry. Zeolites can also remove dyes from the washing liquor by hetero-coagulation and adsorption. Another application of zeolites is separation of ammonia from drinking or wastewater. Ammonia in the environment originates from metabolic, agricultural and industrial processes and from water disinfection with chloramine. The zeolites are very effective for ammonia removal, due to their high selectivity for ammonium ion in the presence of competing cations, such as  $K^+$ ,  $Ca^{2+}$  or  $Mg^{2+}$ . Metals having density higher than  $5\text{ g/cm}^3$  are generally considered as heavy metals. Among the heavy metals Cd, Cr, Cu, Ni, Zn, Pb and Hg are well known with their toxicity and considered as environmentally hazardous. Zeolites have been widely explored for removal of heavy metals from natural or industrial wastewater. The removal efficiency of zeolites depends upon the type and amount of zeolite, contact time, pH, temperature, initial metal concentration as well as on presence of competitive ions.

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## Lecture 37

### Polymerization

Polymers are macromolecules obtained by bonding monomers which are small molecules consisting of unit structure of polymer that are repeated. Polymers with desirable properties of toughness, strength and elasticity have molecular weight in the range of  $10^4$  to  $10^6$  g/mol. Polymer can be classified in different ways :

1. Based on thermal behavior
  - a. Thermoplastic : These polymers soften on heating.
  - b. Thermoset : This class of polymers have rigid three dimensional structure and are not softened on heating.
  - c. Elastomers : These polymers have low crystallinity and high flexibility.
2. Based on structure
  - a. Homochain polymer

These polymers are synthesized from single monomer such as alkene (propylene, vinylchloride, styrene) or dienes (butadienes). Different stereochemical arrangements of substitutional R group around the carbon chain as shown in Fig. 1 result in polymers with variation in properties. In isotactic arrangement substitutional R group lies on the same side of the carbon chain as shown in Fig.1. In syndiotactic form R group alternate on either side of the carbon chain. When there is random arrangement of the substitutional R group on carbon chain the arrangement is known as atactic. The stereoregularity of polymer has significant effect on the properties of polymers. Isotactic and syndiotactic are crystalline where as atactic polymer are amorphous. Polypropylene exists in these forms. Isotactic polypropylene polymer is semicrystalline material while atactic polypropylene has rubber like properties.

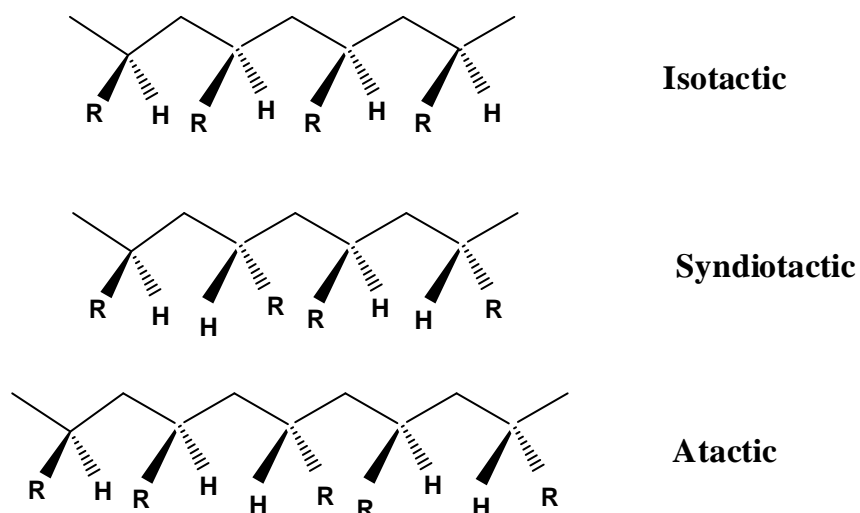


Fig. 1 . Different stereochemical arrangements of homochain polymers

## b. Copolymer

Copolymers are prepared from two or more type of polymers. Different types of copolymers are obtained depending on the sequence of bonding of two different homochain polymers say A and B as shown in Fig. 2. Random copolymers have lower crystallinity and greater elasticity. In block polymer, blocks of one type of homopolymer structure are attached to blocks of another type of homopolymer. As a result in block polymer, desirable properties from each of the co-monomers are obtained. The styrene-butadiene thermoplastic elastomer is an example of block polymer while the acrylonitrile-butadiene-styrene (ABS ) impact polymer is an example of network polymer.

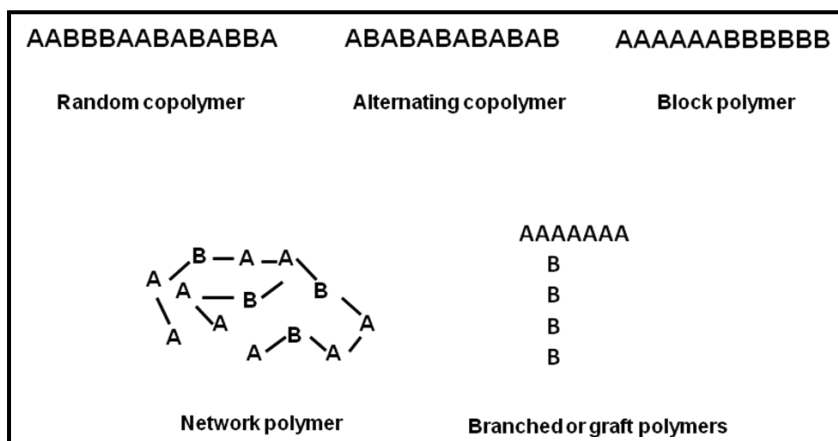


Fig. 2. Different types of copolymers that can be obtained from two homopolymers A &amp; B

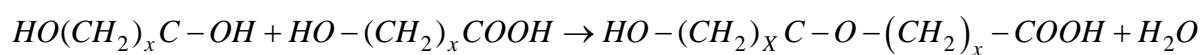
Polymers can be produced by both heterogeneous and homogeneous catalytic processes though most industrial catalysts are heterogeneous. Catalysts are essential for initiation and/or control of the polymerization process. Polymerization processes are different from the other conventional catalytic processes in the fact that the catalysts are rarely recovered unchanged at the end of the reaction. The catalysts generally remain within the products as the separation cost is too high. Typically more than one ton of polymer per gram of catalyst is produced.

Polymerization can be done either by :

1. Step growth (condensation) reaction or
2. Chain growth (addition or insertion) reaction

### Step growth reaction

The step growth reaction involves condensation reaction of two different functions A and B, present on two different molecules. The linkage between the molecules is formed by elimination of smaller molecules such as water, alcohol, HCl, CO<sub>2</sub> and other molecules. For example the polyester oligomer is formed by condensation reaction of an acid function with an alcohol eliminating H<sub>2</sub>O molecule and can react further with either a monomer or an oligomer. Condensation reactions are typically catalyzed by acid, base and/or metal ions.



Polymers such as polyester, polyurethane or polyamides are formed by step growth condensations. Polyester is formed from the reaction of a diacid with a dialcohol catalyzed by toluene sulfonic acid or metal salts. Polyurethane is produced from condensation of di-isocyanate and di-alcohol catalyzed by tertiary amines (1,4 – diazabibicyclo(2,2,2) octane and metal salts while polyamides (nylons) are synthesized by condensation of diamine and diacid.

**Chain growth reaction**

Chain growth polymerization involves reaction of unsaturated monomer compounds such as vinylic, acrylic or dienic or strained heterocyclic monomers. Reaction is initiated by formation of an active site on a monomer and is a slow process. It is followed by rapid propagation by addition of monomers to active sites by opening of double bond or ring. Then there is transfer of active site to macromolecular polymer to end its growth and begin further growth of another. Finally, in the termination step destruction of active sites occurs. The active sites for chain growth polymerization include unpaired electrons as in free radical polymerization, anions having carbon –metal or alkoxide, cations such as carbenium or oxonium ions and co-ordination bonds with transition metals in Ziegler – Natta or metallocene catalysts.

Polymers produced via chain polymerization include polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyvinyl esters, acrylonitrile etc.

**Polymerization catalysts**

As the cost of separation of catalysts from the products is high, polymerization catalysts are usually not recovered at the end of the process. Hence it is essential that catalysts should be non-detrimental to the product quality. The catalysts should also have high activity so that minimum amount of catalyst is needed for the process. This will minimize the amount of catalyst retained within the products.

Commercial polymerization catalysts can be broadly classified as follows :

1. Oxygen containing initiators such as peroxides for free radical polymerization.
2. Speciality acids, bases, metal ion compounds and organometallic complexes for step (condensation) polymerization.
3. Ziegler Natta, metallocene or supported metal oxide catalysts for coordinative and stereo specific polymerization.

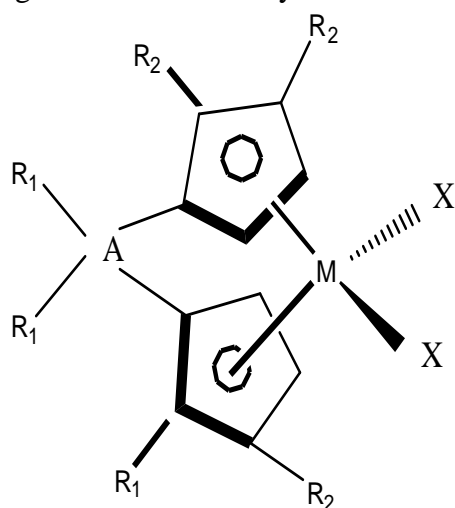
Sometime catalyst additives are used which improve chain transfer, production rate and stereoselectivity in free radical and coordinative polymerization. For example ethyl benzoate is used as additive to improve the catalyst stereo selectivity.

### Ziegler – Natta catalysts

Ziegler – Natta catalysts are prepared from transition metal halides such as chloride or iodide of Ti, V, Zr, Cr, W, Co and aluminum (Mg or Li) alkyl. The titanium catalysts are prepared by the interaction of  $\text{TiCl}_4$  and alkyl aluminium compounds in hydrocarbon solvent. Titanium supported on magnesium salts are also used. For production of polyethylene, poly propylene and polydienes Ti-Al or Ti-Mg complexes are typically used. The homogeneous vanadium based catalysts such as  $\text{VOCl}_3$ ,  $\text{VCl}_4$  or  $\text{VO}(\text{OR})_3$  with aluminum alkyls such as  $\text{RAlCl}_2$  are used for production of polymers by copolymerization. The Ziegler – Natta catalysts are capable of stereoregulation during polymerization reaction and thereby increases selectivity of a particular product. For example Ziegler – Natta catalyzed process is highly selective for linear polyethylene production.

### Metallocenes catalysts

Metallocenes are highly stereo specific catalysts having increasing applications. These catalysts consist of transitions metal (Zr, Ti or Hf) sandwiched between cyclopentadienyl rings to form a sterically hindered site. Typical structure is shown in Fig.3.



M = transition metal Zr, Ti, Hf ;

A= optional bridging atom Si,C ;

$\text{R}_1$  = methyl group ;

$\text{R}_2$  = H, alkyl or other hydrocarbon groups;

Fig. 3. Structure of typical metallocenes catalysts

These catalysts have high activity as well as stereoselectivity. The catalyst can produce either isotactic or syndiotactic polypropylene and are called single site catalyst. Polymers produced by metallocene catalysts have narrow molecular weight distribution. The main limitation of metallocene catalysts is their higher cost compared to conventional Ziegler – Natta catalyst. But due to higher activity and gradually decreasing price scenario metallocene based industrial polymerization process are rapidly growing.

### **Supported metal oxide catalyst**

Most industrial polymerization catalysts are supported. Supported metal oxide catalysts include Cr, Mo, Co or Ni supported on alumina, silica, zirconia and activated carbon. They are used commercially for low pressure polymerization of alkene. The most active catalysts are Cr/SiO<sub>2</sub>, Zr/Al<sub>2</sub>O<sub>3</sub> and Ti/MgO. These catalysts are observed to be active for ethylene polymerization but are less effective for propylene production because of low stereoregularity.

Chromium catalysts are extensively used in production of high density polyethylene HDPE. These catalysts are of two types; supported chromium oxide and organometallic compounds such as bis(arene)Cr<sup>0</sup>. Chromium oxides are supported on silica, alumina or titania. The supports affect the molecular weight distribution. Sometime mixed composition of inorganic and organic catalysts are also used.

The supported catalysts are rapidly poisoned, fouled or encapsulated by the polymer product. To maintain catalyst activity, the catalyst must constantly undergo fragmentation to expose new active catalytic sites.

### **Text References**

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## Lecture 38

### Fragmentation of polymerization catalysts

Many industrial polymerization reactions are carried out with supported catalysts. Typically porous silica,  $\text{MgCl}_2$  or certain polymers are used as supports. For supported catalysts on initiation of polymerization, the active sites on the catalyst surface are rapidly fouled due to encapsulation by the polymer product. However, the catalyst may undergo fragmentation due to accumulation of polymers within the catalyst particles. This fragmentation results in exposure of new active catalytic sites and maintains the catalytic activity. The fragmentation process ensures access of the monomers to the active catalyst sites. The fragmentation of catalyst particles are typically observed for olefin polymerization reactions such as polyethylene and polypropylene productions with Ziegler–Natta catalysts. Fragmentation of catalyst particles results in higher polymer yield. Since recovery of the catalyst particles from polymer product is difficult and expensive, fragmentation of catalyst makes the catalyst particles small enough so that final product quality is not affected. In the final product, the size of the catalysts particles are in the range of  $\sim 100$  nm which are embedded in large polymer particles of  $200 - 1000$   $\mu\text{m}$  diameter.



## Fragmentation and polymer growth models

### 1. Core – shell model

According to this model, catalyst particles do not break up in the beginning of the polymerization process. Initially, polymerization occurs on the surface of the particle which acts as a core. Then, the polymer grows in the form of a shell around the core. After formation of accumulated polymer shell, the monomer has to diffuse through the polymer layer to reach the catalyst surface, where it reacts. The model is more applicable for catalysts with low porosity for which monomer diffusion is limited

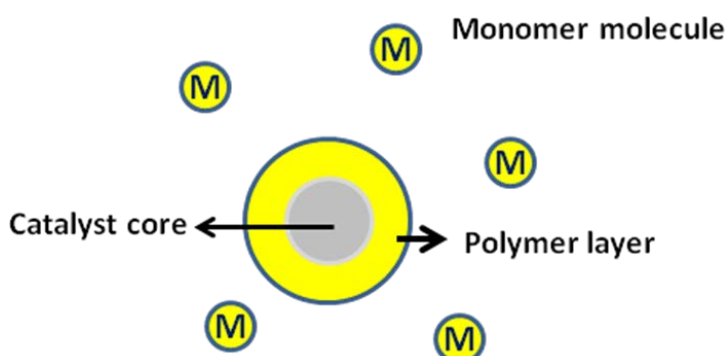


Fig. 4. Core – shell model for polymer growth

### 2. Multigrain model

For highly porous catalyst monomer diffusion is less limited and monomer can penetrate into the pores of the catalyst more easily. Consequently polymer can grow throughout the particle and result in immediate fragmentation of the catalyst particles (Fig. 5).

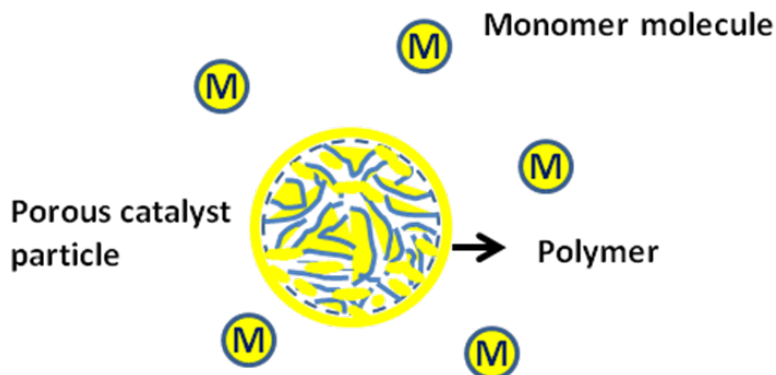


Fig 5. Growth of polymer within the pores of porous catalysts

After initial breaking of catalyst particles into small fragments (microparticles), polymerization reaction occurs on surface of microparticles according to core-shell model. These microparticles together form porous macroparticles. This is the most accepted model for particle growth in olefin polymerization. Scheme of polyethylene morphology development during gas phase polymerization is shown in Fig. 6.

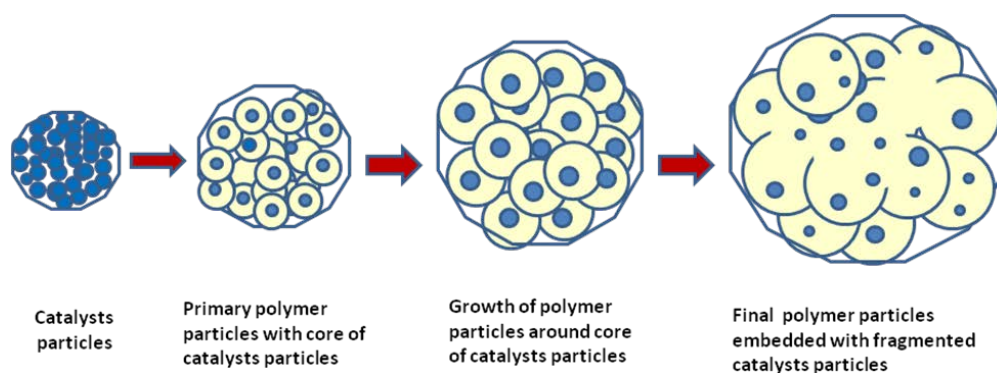


Fig. 6. Scheme of development of polymer with catalysts fragmentation

Several researchers have studied fragmentation of Ziegler–Natta catalyst for olefin polymerization. The fragmentation behavior of the emulsion-based Ziegler–Natta catalyst for propylene polymerizations was observed to be faster and more uniform than that of the  $\text{MgCl}_2$ -supported and silica-supported catalysts of similar chemical composition [1-2].

### Liquid phase polymerization

Radical polymerizations can be carried out both by homogeneous and heterogeneous process depending on whether the initial reaction mixture is homogeneous or heterogeneous. Bulk polymerization and solution polymerization are homogeneous processes while suspension and emulsion polymerization are heterogeneous processes. By heterogeneous polymerization thermal and viscosity problems can be controlled more efficiently.

## 1. Bulk polymerization

Bulk polymerization of pure liquid monomer is the simplest process and carried out by using initiator in the absence of diluent or solvent. For this process reaction rate is high due to high monomer concentration and result in high yield per volume of reactor. Another advantage is that the relatively pure product is produced. However, control of the bulk polymerization, exothermic in nature, is difficult. The viscosity of the reaction system increases rapidly even at relatively low conversion. The heat removal is difficult due to high viscosity and low thermal conductivity of the polymer melt. Consequently local hot spots may occur resulting in degradation and discoloration of the polymer product. Bulk polymerization requires careful temperature control and strong elaborate stirring equipment. Though, bulk polymerization is commercially less used, polymerization of ethylene, styrene and methyl methacrylate are carried out by this method. The heat dissipation and viscosity problem are reduced by carrying out polymerization at low conversion. Bulk polymerization can be carried out in conventional stirred tank reactor, long tubular reactor with high surface to volume ratio and screw extruder reactors.

## 2. Solution polymerization

Solution polymerization of monomers is carried out with dissolved monomers and initiators in solvent. Typical solvents include aromatic and aliphatic hydrocarbons, esters, ethers, alcohol or water. The solvent acts as diluent and aids in transfer of the heat of polymerization. In presence of solvent the stirring becomes easier since the viscosity of the reaction mixture is decreased. Consequently controlling of process temperature is much easier in solution polymerization compared to bulk polymerization. However, in presence of solvent purity of the product is reduced particularly if there is a difficulty in removal of solvent. Vinyl acetate, acrylonitrile and ester of acrylic acid are polymerized in solution.

### 3. Suspension polymerization

Suspension polymerization is carried out by suspending relatively large droplets (10-1000 $\mu\text{m}$ ) of insoluble monomers along with catalyst in water. The water to monomer weight ratio varies from 1:1 to 4:1 in most polymerization. The monomer droplets are prevented from coalescing by agitation and presence of stabilizers. The suspension stabilizers are typically used in less than 0.1 wt% of the aqueous phase. Two types of stabilizer are used :

1. Water soluble polymers such as poly vinyl alcohol, sodium poly styrene sulfonate, hydroxypropyl cellulose etc.
2. Water insoluble inorganic compounds such as talc, barium sulfate, kaolin, calcium phosphate etc.

Styrene , acrylic and methacrylic esters , vinyl chloride, vinyl acetate and tetrafluoro ethylene are polymerized by suspension method.

### 4. Emulsion polymerization

Emulsion polymerization involves finely divided droplets of insoluble monomers suspended in water. Hydrophobic monomer droplets, of diameter in the range of 0.5 -10  $\mu\text{m}$ , are dispersed in water which also serves as heat transfer medium. In emulsion polymerization water soluble initiators such as persulphates are used. The difference between emulsion polymerization and suspension polymerization lies in the type and size of the particles in which polymerization occurs and kind of initiator employed. Many industrial polymers are produced by emulsion polymerization such as polybutadiene and PVC.

### Gas phase polymerization

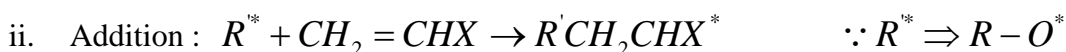
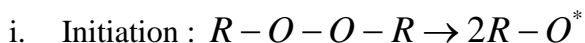
Large scale production of polyethylene and polypropylene from gaseous monomer is carried out using heterogeneous catalyst. Powdered catalysts are mixed with gaseous monomers at the reactor entrance. Reactors are fluidized bed or stirred reactors. The major advantage of this process is that monomers can be easily separated from polymers. Catalyst residues are not separated from polymers.

## Coordination polymerization

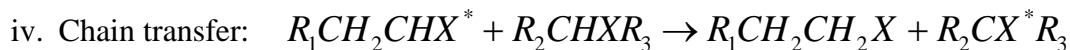
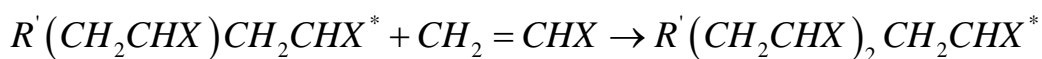
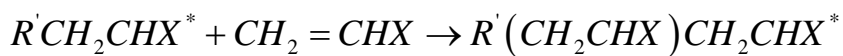
The polymerization catalyzed by transition metal complex such as Ziegler-Natta catalysts or metallocene catalysts is also known as coordination polymerization. The Ziegler – Natta catalysts system may be heterogeneous (some titanium based system) or soluble (most vanadium containing species). The best known are derived from  $\text{TiCl}_4$  or  $\text{TiCl}_3$  and aluminium trialkyl. These catalysts are highly stereospecific and can orient the monomer in specific direction before addition to the chain. The Ziegler-Natta and metallocene initiators are considered as coordination initiators that perform stereoselectivity by coordination. The olefin polymerization is carried out in presence of Ziegler–Natta catalyst ( $\text{TiCl}_4$  supported on  $\text{MgCl}_2$ ).

## Mechanism and rate

Radical chain polymerization involves initiation, propagation, termination, chain transfer and inhibition. For free radical polymerization the mechanism of formation of polymer using peroxide catalysts can be represented as follows:

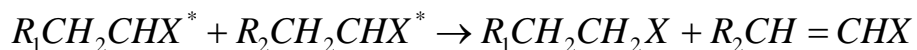


iii. Propagation :



v. Termination

:



Assuming that (a) overall rate of reaction is determined by rate of propagation and (b) rate of initiation of free radical is equal to rate of their termination, the overall rate equation can be derived as :

$$r_{overall} = k_{prop} \left( \frac{f k_{init}}{k_{term}} \right)^{0.5} C_M C_I^{0.5}$$

$C_M$  = concentration of monomers

$C_I$  = concentration of initiators

$k_{prop}$  = rate constant for propagation

$k_{init}$  = rate constant for initiation

$k_{term}$  = rate constant for termination

$f = 2$  (for given mechanism) = ratio of initiators  $R^*$  formed by initiation reaction to that consumed in subsequent addition reaction

The coordination polymerization on Ziegler–Natta catalyst is assumed to be initiated by adsorption of monomer at an electron deficient surface vacant site on octahedral structure of titanium metal alkyl complex. A transition complex is formed by opening of the double bond. The complex is then rearranged by insertion of the monomer into the growing chain. When the insertion occurs at the original chain growing site with respect to metal ion and original vacant site is retained then the growth corresponds to isotactic growth. However if the chain growth site and vacant site interchange, then the chain growth corresponds to syndiotactic growth. The mechanism is shown in Fig. 7.

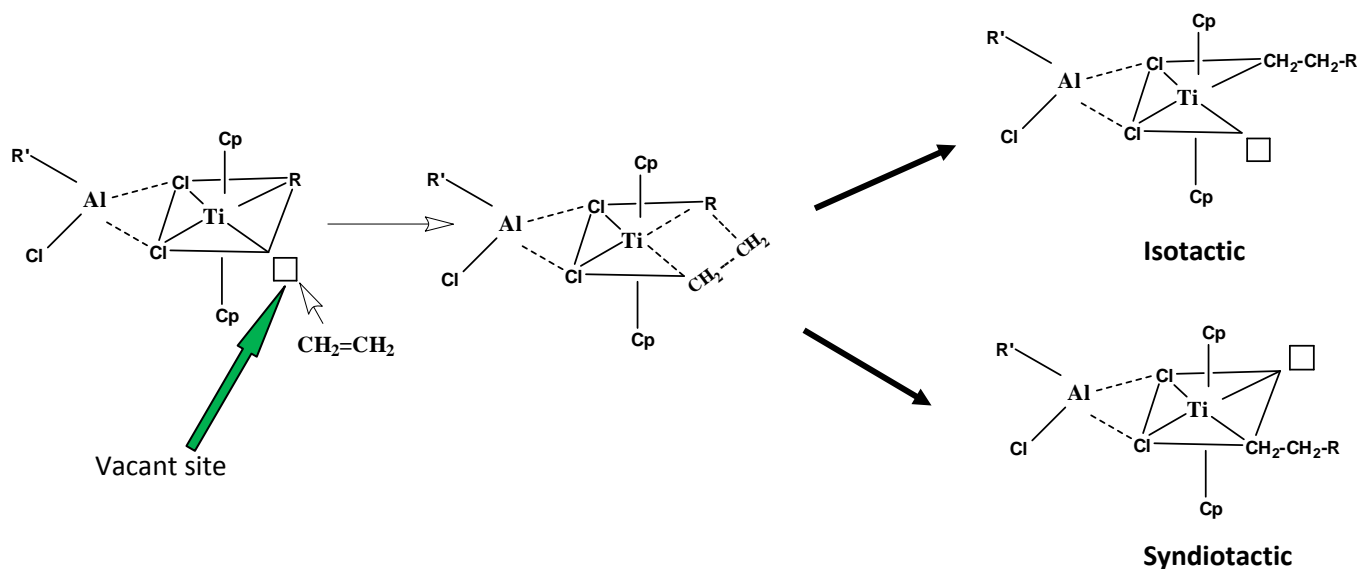
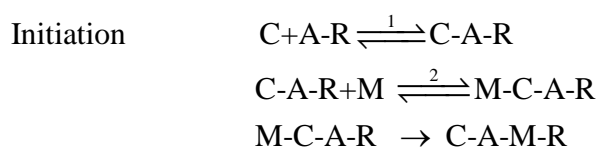


Fig. 7. Polymerization of ethylene with Ziegler-Natta catalysts

The Ziegler Natta catalysts are mostly heterogeneous in nature and adsorption processes are most likely to occur during polymerization reactions. Various kinetic schemes have been proposed assuming that polymerization centers are formed by the adsorption of metal alkyl species on the surface of a crystalline transition metal halide and then chain propagation occurs between the adsorbed metal alkyl and monomers. Langmuir Hinshelwood rate law for adsorption and reaction on solid is frequently adopted for this kind of reaction scheme. The rate expression for the heterogeneous Ziegler–Natta catalyzed polymerization process can be derived by using following model.



C = transition metal complex

A-R = metal alkyl

M = monomer

Assuming the rate of initiation and termination to be equal and that the overall rate is summation of rate of propagation and transfer, the overall rate can be derived as:

$$-\frac{dC_M}{dt} = \frac{(k_{prop} + k_{transfer})k_{init}}{k_{term}} \left[ \frac{(K_1 C_{AR})(K_2 C_M)}{(1 + K_1 C_{AR} + K_2 C_M)^2} \right]$$

$k_{init}$  = rate constant for initiation

$C_M$  = concentration of monomers

$k_{prop}$  = rate constant for propagation

$C_{A-R}$  = concentration of metal alkyl

$k_{transfer}$  = rate constant for transfer

$K_1$  = equilibrium constant for step 1

$k_{term}$  = rate constant for termination

$K_2$  = equilibrium constant for step 2

## Industrial processes

Most polymerization processes are carried out in the liquid phase in batch reactor or CSTR and only few are continuous. For continuous process plug flow or fluidized bed with low residence time is used. Long residence time should be avoided in batch /CSTR as it is associated with many disadvantages such as catalysts decay and accumulation, polymer degradation, production of non-uniform polymer etc.

### 1. Polyethylene production (PE)

Different grades of polyethylene such as low density polyethylene (LDPE), high density polyethylene (HDPE) or linear low density polyethylene (LLDPE) are produced commercially.

#### Low density polyethylene (LDPE) and high density polyethylene (HDPE)

The LDPE or high pressure polyethylene is produced by radical polymerization. The HDPE or low pressure polyethylene is synthesized by co-ordination polymerization. Except LDPE, all other polymers of olefins are produced by co-ordination catalysts. LDPE obtained by radical polymerization differs structurally from HDPE produced by traditional Ziegler Natta co-ordination catalyst. The LDPE is more highly branched (both short and long branch) than HDPE and is therefore lower in crystallinity and density. The crystallinity of LDPE lies in the range of 40-60% and while that of HDPE in 70-90% . The density of LDPE and HDPE lie in the range 0.91 -0.93 g/cm<sup>3</sup> and 0.94-0.96 g/cm<sup>3</sup>



respectively. Compared to LDPE, HDPE has increased tensile strength, stiffness, chemical resistance and upper used temperature. Most HDPE have number average molecular weights in the range of 50000 -250,000 and have wide range of applications such as bottles, housewares, toys, pails, film for grocery bags and food packing, pipe, tubing, cables etc.

### **Linear low density polyethylene (LLDPE)**

Co-ordination copolymerization of ethylene in presence of small amount of  $\alpha$ -olefins such as 1-butene, 1-hexene or 1-octene results in polyethylene that have structure, properties and applications equivalent to the branched LDPE produced by radical polymerization. This polyethylene is known as linear low density polyethylene (LLDPE) and has controlled amount of ethyl, n-butyl and n-hexyl branches respectively.

The polyethylene can be produced by following methods :

- i. LDPE is produced by free radical high pressure bulk polymerization process
- ii. HDPE and LLDPE are produced by slurry-suspension process at moderately low pressure. The process is carried out over supported catalysts such as supported Cr or Cr organometallic or coordination catalysts such as metallocene or Ziegler –Natta catalysts. The reaction conditions are 80- 150  $^{\circ}\text{C}$  and 20-35 atm pressure. Supported catalyst is typically suspended in alkene or cyclohexane solvent which also serve as the heat transfer medium. The Ziegler–Natta( $\text{TiCl}_4/\text{Al}$  - alkyl/ $\text{MgCl}_2$  ) catalyst is more active than Cr based catalysts.
- iii. HDPE and LLDPE can also be produced by gas phase fluidized bed polymerization over supported  $\text{CrCO}_3$  or Ti based catalysts.

## 2. Polypropylene production

Isotactic isomers of polypropylene are most useful. It is stronger and harder than polyethylene and frequently used in block copolymer production. Various catalysts are used for this process.

- a. Using Zeigler – Natta catalyst : The process is carried out at 70 °C and ~13 atm using slurry reactors. Catalyst are prepared by reducing  $\text{TiCl}_4$  with  $\text{Al}(\text{C}_2\text{H}_5)_3$  in a cold hydrocarbon liquid to produce stereo-unselective form of  $\text{TiCl}_3$ . On heating to 100-200 °C,  $\text{TiCl}_3$  form convert to the stereo-selective form. Isotactic yield of propylene is about 92 %. The final active catalysts contain  $\text{TiCl}_3$  and  $\text{AlCl}_3$ .
- b. Using  $\text{MgCl}_2$  supported  $\text{TiCl}_3$  catalyst : The process is carried out at 70 °C and 13-20 atm pressure. It gives around ~ 95 % isotactic polypropylene yield. The catalyst is prepared by first milling  $\text{MgCl}_2$  with ethy bezanoate extensively to produce a highly active disordered state. Then it is treated with  $\text{TiCl}_4$  at 100 °C .
- c. Metallocene catalysts are more active with higher stereo selectivity. 100 % yield of isotactic or syndiotactic is possible.

**Deactivation:** CO, O<sub>2</sub> and S compounds act as poison for the catalysts. Reactants are passed through molecular sieve adsorbent column before treating with catalysts.

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## Lecture 39

### Carbon nanotubes (CNT)

Materials with nano sized channels such as carbon nanotubes have received significant attention in recent years. In heterogeneous catalysis CNTs are being investigated as nano reactors, supports, active components and adsorbents. Other applications include electronic devices, gas and biosensors, nano-balance, scanning probe tips etc.

Carbon nanotubes were discovered in 1991 as minor byproduct during synthesis of fullerene which is an allotrope of carbon, in which the atoms are arranged in closed shells. Fullerenes consist of 20 hexagonal and 12 pentagonal rings as the basis of an icosahedral symmetry closed cage structure. The structure is shown in Fig 1.

Carbon nanotube structures consist of graphene cylinders closed at either end with caps containing pentagonal rings.  $C_{70}$  is smallest nanotube. Nanotubes are formed by rolling up a graphene sheet into cylinder and capping each end with half of a fullerene molecule. Different wrapping results in different structures (Fig. 1) and electronic properties.

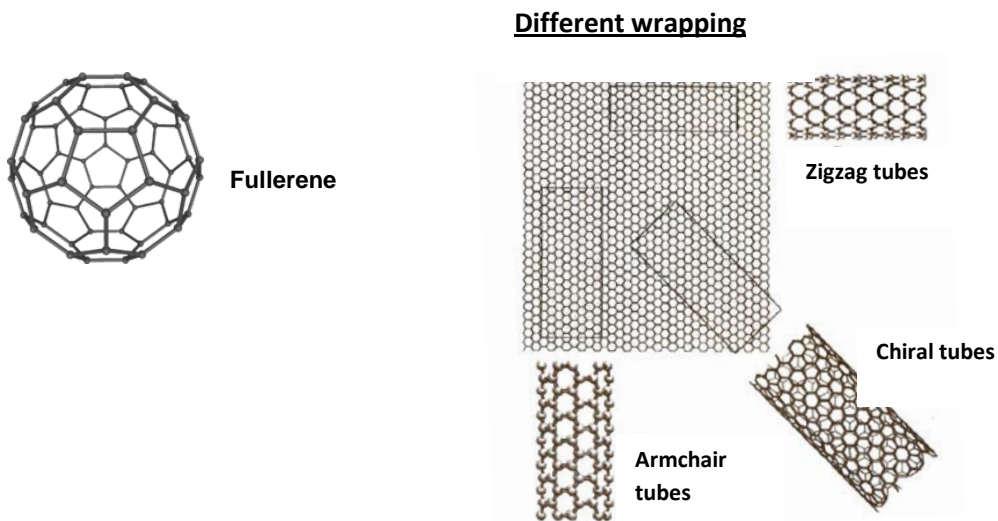


Fig. 1 : Structures of fullerene and carbon nanotube

In zigzag tubes some of the C-C bonds lies parallel to tube axis and in armchair tubes few C-C bonds lies perpendicular to tube axis. Chiral tubes have intermediate orientation.

## Types of CNTs

Carbon nanotubes are of two types :

- i. Single wall carbon nano tube (SWNT)
- ii. Multiple wall carbon nano tube (MWNT)

Single wall nanotube (SWNT ) consist of one cylinder. It is made of single graphene sheet rolled up into cylinder closed by two caps (semi fullerenes). The SWNTs have diameter in the range of 0.5 -2.0 nm. The length is in the range of 50-150  $\mu\text{m}$  length. The SWNTs are microporous and the specific surface area is in the range of 1300  $\text{m}^2/\text{g}$  (outer surface). SWCNTs are commonly arranged in bundles. SWNTs have less topological defects and have better mechanical and electro physical properties. Electronic properties of SWNTs are governed by two factors, tube diameters and helicity, which further depend on the way graphene layer is rolled up, arm chair or chiral. Armchair SWNTs shows conductivity as similar to metal whereas zigzag SWNTs behave as semiconductors. In catalysis CNTs have high application as support. Electrical conductivity, surface curvature and presence of inner cavity in CNTs make the metal – support interaction different compared to that in activated carbon or graphite support. Mechanically bent SWNTs present kink sites that are chemically more active. Metal nanoparticles size depends strongly on metal-CNT interactions with stronger interaction giving rise to smaller nanoparticles. Studies have shown that convex surface of CNTs are more reactive than concave surface and the difference in reactivity increases when the tube diameter decreases.

Multiwall (MWNT) nano tubes consist of many nested concentric SWNTs cylinders with increasing successive radii. The concentric walls are spaced regularly at 0.34 nm similar to inter graphene distance. MWNTs have outer diameter in range of 2 – 100 nm depending on number of coaxial tubes present. MWNTs are usually mesoporous in nature and specific area depends on the number of walls. The length of MWNTs can range from few to hundreds  $\mu\text{m}$ . The advantage of MWNT over SWNT is that the multi-shell

structures of MWNTs are stiffer than single wall hence stability is higher. Also large scale synthesis of MWNT is possible by various methods. The most common characterization techniques of these materials are electron microscopy, Raman spectroscopy, TGA , IR and UV-Vis.

## Synthesis of CNT

There are two main methods for preparation of CNT

### 1. Sublimation of graphite with subsequent desublimation

This method involves condensation of carbon atoms generated from evaporation of solid carbon sources of graphite. The sublimation of the solid can be done using electric arc or laser ablation (Fig. 1) where the temperature reaches to 2500 -3500 °C.

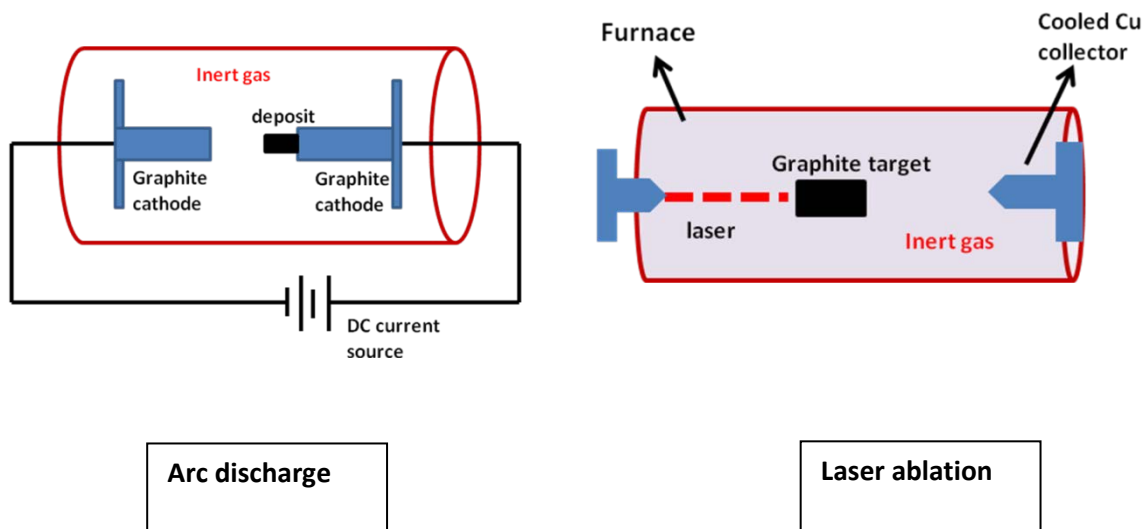


Fig. 2. Schematics for CNT formation by sublimation of graphite with subsequent desublimation.

The electric arc discharge method is one of the efficient techniques for synthesis of CNT. Typically, about 60 to 70 wt% of the arc-synthesized soot is CNT. The rest of the soot comprises of fullerenes, amorphous carbon and catalyst nanoparticles. In electric arc discharge production of CNT two graphite rods are used and a current is passed continuously between the electrodes. The anode is drilled and filled with catalysts. The metal oxides (Ni, Co, Fe) are used as catalyst. In some cases the catalyst/graphite composite is used as electrode. The synthesis is performed in a cooled chamber in the presence of helium, argon or methane environment. During the arcing, the catalyst/graphite anode

is evaporated and consumed with simultaneous carbon deposition around the cathode. The quality of CNT samples depends upon arc stability, current density and cooling of cathode. In laser ablation method the graphite target is subjected to laser and sublimated carbon is recollected. Inert gas atmosphere is maintained within the chamber.

## 2. Decomposition of carbon containing compounds

The most used method to prepare CNT is pyrolysis of hydrocarbon gases or vapors such as propane, butane, hexane, benzene, toluene etc. The method is also known as chemical vapor deposition (CVD) process.

### Chemical Vapor Deposition (CVD)

By chemical vapor deposition CNTs can be produced in large quantities. The process temperature can vary from 500 – 1300 °C. The hydrocarbon precursors include CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, alcohols etc.

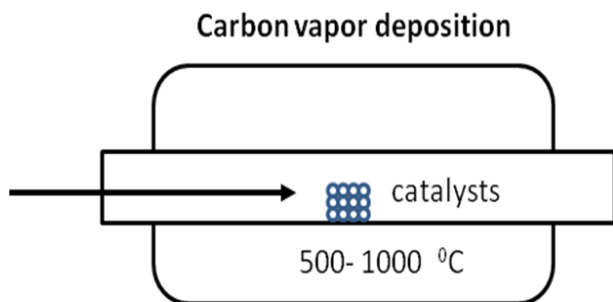


Fig. 3 . Schematics for carbon vapor deposition method

In CVD method there is initial dissociation of hydrocarbons followed by dissolution and saturation of C atoms in metal nanoparticles. Thereafter there is precipitation of carbon. Vapor-grown CNTs generally use metal catalyst particles. Fe, Co and Ni catalysts are mostly used for the catalytic growth of CNT. More recently, CNTs have also been grown from metal such as Au, Ag and Cu. Catalyst serves as nucleation sites and also promotes pyrolysis of hydrocarbons.

**Growth Mechanisms :**

The growth mechanism of CNT on metal based catalysts and nonmetal based catalysts are discussed below.

**i. metal based catalysts**

The growth mechanism of CNTs is yet to be fully established. In general it is proposed that hydrocarbons adsorb on metal particles and are catalytically decomposed. This results in carbon dissolving into particle. Upon supersaturation, carbon precipitates in tubular crystalline form. However, various alternative models have been proposed and appropriate description of growth depends on synthesis route and conditions used. Two most described models are root growth and tip growth [1]. The growth mechanisms are schematically explained in Fig. 4. For formation of CNTs the metal catalysts have to be dispersed well on the substrate forming nano clusters on the substrate surface. When there is a strong interaction between the catalyst clusters and substrate, the CNT grows by the root-growth mechanism. The pyrolysis of hydrocarbons produces the carbon atoms which are extremely mobile on metal surfaces and rapidly diffuse over and through the metal particles. The graphite precipitates around the catalyst particles and cylindrical structures are formed in a nested fashion from the catalyst particle, with the catalyst particle at the root. The growth of the nanotubes stops when the catalyst particles are completely covered with layers of carbon. The tip growth mechanism is observed when the interaction between metal catalyst clusters and substrate is weak. Due to the weak interaction, the catalyst particles are lifted off the substrate by the cylindrical structures formed below it. While, the carbon nanotube base remains anchored to the substrate, the tip carrying the catalyst particle grows toward the region of higher feed gas concentration. The tip growth stops when the catalyst particle is covered with carbon layers or when the supply of feed gas is cut off.

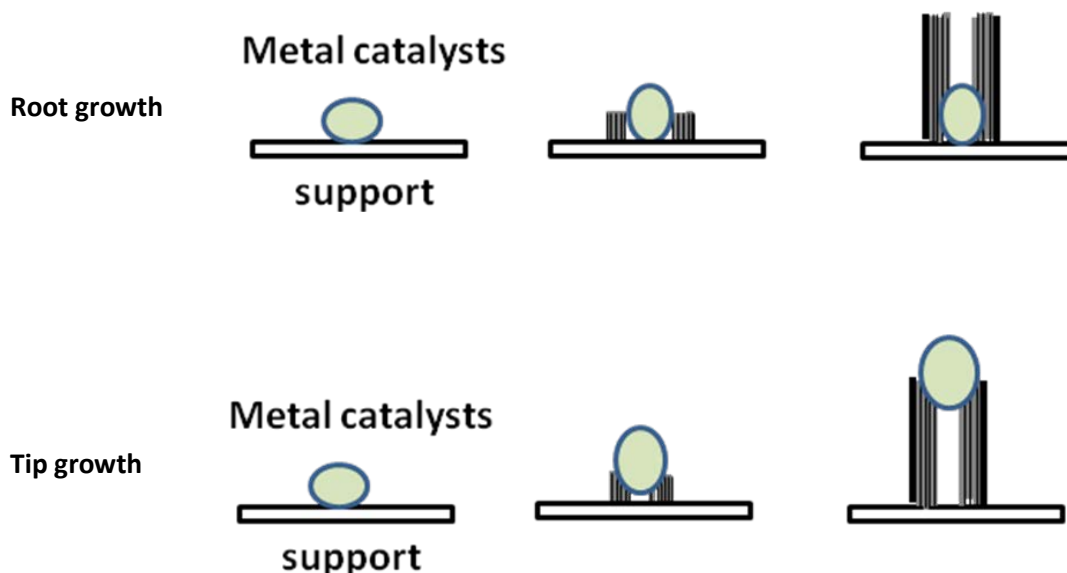
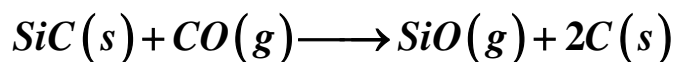


Fig. 4. Schematics showing root growth and tip growth mechanism of CNTs

Synthesis of carbon nanotubes over Fe catalyst on aluminium is described by Emmenegger et al. [2] as follows. Initially the iron nitrate layer formed on the support transforms to crystalline  $\text{Fe}_2\text{O}_3$  film during heating under nitrogen. After acetylene is introduced,  $\text{Fe}_2\text{O}_3$  film is fragmented and smaller particles are formed.  $\text{Fe}_2\text{O}_3$  crystals are reduced to inter-mediate oxides such as  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$  by hydrogen released from pyrolysis of acetylene. Finally metastable  $\text{Fe}_3\text{C}$  is formed and growth of CNT occurs by tip growth mechanism.

ii. **Non-metal based catalysts** (Ceramic and semiconductor catalysts)

Among non-metallic catalysts SiC is most widely used. The Fig.5 shows the carbon nanostructure formation over silicon carbide by carbothermal reduction of silica. At first stage  $\text{SiO}_2$  is reduced to SiC via a carbothermal reaction. In next step SiC nano particle coalesce and finally carbon nanotube growth occurs on surface of SiC particles through carbon precipitation and/or SiC decomposition. The carbon generation reaction is given below.





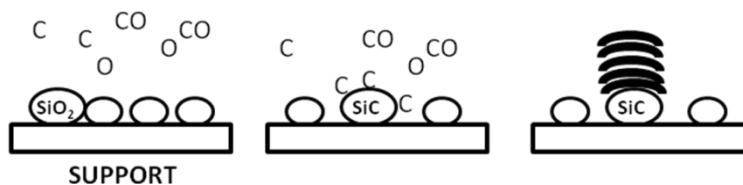


Fig. 5. Schematic representation of CNT formation over silica

MgO, Al<sub>2</sub>O<sub>3</sub>, zirconia, magnesium borates etc. are also reported to be used to grow carbon nanotubes.

### Characterization of CNT

X-ray diffraction pattern of CNTs are close to graphite. A graphite-like peak (002) is present and measurements of interlayer spacing can be obtained from its position using the Bragg law [3]. Carbon nanotubes are also active in Raman spectroscopy [3]. Most characteristic features are : peak  $<200\text{ cm}^{-1}$  which is characteristic of SWNT, frequency depend on tube diameter. The  $1340\text{ cm}^{-1}$  is assigned to residual ill-organized graphite. The  $1500 - 1600\text{ cm}^{-1}$  peak also characteristic of nanotubes. The TEM images are essential for studying CNTs.

### Application of CNT and CNT based catalysts

CNTs are used in several catalytic reactions as catalyst or catalyst supports. In particular liquid phase reactions were studied extensively with MWNT. Higher surface area and mesoporous nature resulted in significant decrease in mass transfer limitations compared to activated carbon.

#### 1. Hydrogenation reactions

This is one of the most studied catalytic reactions both in liquid and gaseous phases. Ni, Rh, Ru supported on CNT were reported to be more active for hydrogenation reactions compared to when supported on activated carbon. Hydrogenation reactions such as hydrogenation of alkenes and  $\alpha,\beta$  – unsaturated aldehyde have been reported for CNT supported catalysts. Ruthenium nanoparticles supported on MWCNTs showed excellent catalytic activity for hydrogenation of aromatic hydrocarbon. The 5wt% Pt/CNT catalyst

was reported to be significantly more active than 5wt% Pt/AC for hydrogenation of trans-diphenylethene and trans  $\beta$ -methylstyrene [4]. Rhodium complex grafted on MWCNTs was reported to be very active for cyclohexene hydrogenation [5] while Pd/CNT catalyst was found to be active for benzene hydrogenation [6]. Pt supported on SWCNTs has been found to be active and selective in hydrogenation of prenal (3-methyl-2-butenal) to prenol (3-methyl-2-butenol) [7].

## 2. Reaction involving CO/H<sub>2</sub>

CNTs have been investigated for Fischer –Tropsch reactions, methanol and higher alcohol synthesis and hydroformylation reactions. Copper promoted Fe/MWCNT catalyst are active for Fischer-Tropsch synthesis with olefins [8]. Co-Re/Al<sub>2</sub>O<sub>3</sub> deposited on MWCNT by dip coating exhibited an enhancement in Fischer-Tropsch activity than observed with a similar system without CNT arrays [9]. MWCNTs also have been used as promoter for Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts for methanol synthesis using H<sub>2</sub>/CO/CO<sub>2</sub> [10]. The complex [HRh(CO)(PPh<sub>3</sub>)<sub>3</sub>] has been grafted onto MCWNTs and used for hydroformylation of propene. Higher conversion and higher regioselectivity toward n-butanaldehyde have been reported for CNT supported catalysts compared to that activated carbon or carbon molecular sieve supported catalysts [11].

## 3. Ammonia synthesis and decomposition

The Ru/C catalyst is studied as an alternative to conventional iron based catalyst for ammonia synthesis at high pressure and temperature. However, Ru/C catalyst is prone to deactivation due to metal sintering, metal leaching or methanation of support. The stability of the catalyst are reported to increase on using CNT as support. Ru-K/MWCNT catalyst has been found to be significantly more active than Ru supported on other carbon supports [12]. The catalytic decomposition of ammonia to generate CO- free hydrogen for fuel cells is receiving increasing attention since the process is more economical than using methanol as hydrogen source. The MWCNT supported ruthenium was found to be more active than MgO, TiO<sub>2</sub> or alumina supported Ru [13].

#### 4. Polymerization

The CNTs have excellent thermal and electrical conductivities and reported to be used as fillers in polymer based advanced composites. However due to poor solubility of CNTs, homogeneous dispersion is difficult task. The polymer functionalized CNTs are prepared following three approaches :

- a. A non-covalent functionalization method in which polymers are produced by ring opening metathesis polymerization. The coating of hyper branched polymers on MWCNTs has been obtained via cationic ring opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane with a  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  catalyst [14]
- b. A covalent functionalization performed by, first grafting polymerization initiators onto the tubes through covalent bond and then exposing these CNT based macro-initiators to the monomer. The polymer is obtained by atom transfer radical polymerization. The polyethylene-MWCNT composite has been produced using catalyst grafting procedure by polymerization of ethylene on  $[\text{ZrCl}_2\text{Cp}_2]$  MAO/MWCNT where  $\text{C}_p = \text{C}_5\text{H}_5$  and MAO = methylaluminoxane [15].
- c. Olefin polymerization via anchored metallocenes catalysts. It has been proposed that MWCNT play a key role in increasing the molecular mass. Supporting the catalytic system on MWCNTs increases the polymerization rate of ethylene. Syndiotactic polypropylene-MWCNT composites have been prepared by propylene polymerization on zirconocene-MAO catalysts [16].

#### 5. Fuel cell electrocatalysts

CNTs are used as catalysts supports for anode or cathode catalysis in direct methanol fuel cells or proton exchange membrane fuel cells. The structure and properties of carbon supports which constitute the electrode material have a direct impact on performance of fuel cells. The most studied reactions are methanol oxidation (anode catalyst), oxygen reduction (cathode catalyst) and hydrogen oxidation (anode catalyst). The Pt is most used metal followed by Pt-Ru system. The general observation is that CNT based catalysts are more active and better resistant to poisoning compared to conventional carbon black support. The advantage of CNT supports for fuel cell applications is attributed to :

- a. Higher metal dispersion and higher electroactive surface area
- b. Higher mesopores 3D network facilitating mass transport
- c. Excellent conducting properties which improve electron transfer

## **6. Other applications**

CNT is also being investigated as support for biocatalysts. CNTs have been used for enzyme immobilization which increases enzyme stability, control of pore size, multiple active sites and reduced mass transfer limitations.

CNTs have also been used as direct catalyst for some specific reactions such as methanation to produce CO and CO<sub>2</sub> free hydrogen, oxidative dehydrogenation of ethyl benzene to styrene and oxidative dehydrogenation of propane to propene, selective oxidation of H<sub>2</sub>S, oxidation of aniline, esterification and hydroxylations.

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## Lecture 40

### Nano metal or metal oxide catalysts

Nano particles consisting of small metal or metal oxide crystallites in the range of few nanometers (1-100 nm) are important for catalysis and adsorption. Nanoparticles have higher effective surface area and improved physico-chemical properties giving better performance. Uniform shape and sized catalysts are particularly important for structure sensitive reactions where different type of surface metal atoms such as corners, edges or terrace atoms possesses quite different properties.

Menezes et al. [1] studied the effect of particle size on catalytic activity of titania supported Au-Ag (1:1) nanoparticles for CO oxidation. They observed that reactivity of the catalysts increased as size of the nanometals decreased. They reported turn over frequency of 0.02, 0.04 and 0.08 s<sup>-1</sup> for nanoparticles having average size of 3, 12 and 19 nm respectively.

#### Synthesis of nanoparticles

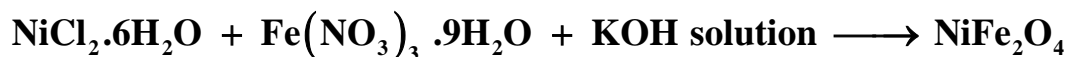
It is a challenge to prepare nanoparticles of uniform shape and size by conventional methods. Various new preparation methods are reported that give nanoparticles with narrow size distribution. Some of the reported methods are :

- Hydrothermal technique
- Microwave assisted synthesis
- Dendrimer assisted method
- Reverse micelle method
- Chemical vapor deposition

### Hydrothermal method

In a hydrothermal process precursor solution, often in presence of an alkali, is autoclaved at certain temperature for specific time. In a typical process, aqueous solution of precursor and KOH is mixed and placed in teflon-lined stainless-steel autoclave. Autoclave is maintained at 70- 200 °C for 10-24 h depending on process and then air-cooled to room temperature. Resulting precipitate is collected by filtration, washed and finally dried.

For example, nickel ferrite particles prepared by hydrothermal process resulted in particles of size distribution from 40-90 nm as reported by Cheng et al. [2] .



### Microwave-irradiated synthesis

Microwave irradiated synthesis method is a new promising technique for the preparation of size controlled metallic nanostructures. Xu et al. [3] reported preparation of Pt nanoparticles supported on CNTs. In this method solutions of Pt precursor ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), ethylene glycol and KOH are mixed in vial and CNTs are uniformly dispersed in mixed solution. Closed vial is then placed in microwave oven (2450 MHz, 800 W) and heated for the required time. The resulting suspension filtered and dried at 120 °C. This preparation method resulted in Pt nanoparticles on surface of CNTs having uniform spherical shape with diameter of  $15 \pm 3$  nm.

### Dendrimer assisted synthesis

Dendrimer is highly ordered branched poly-amidoamine macromolecule with tree-like topology and is used in preparation of nano-material. Dendrimer have multiple coordination sites that are utilized to coordinate metal ions and synthesize metal clusters. In this method metal ions in solution are complexed to dendrimer, mostly with amine groups in the outer shell of OH-terminated poly-amidoamine. Complexed metal ions are subsequently reduced to metal atoms which agglomerate into metal particle. Men et al.

[4] reported synthesis of dendritic polyphenylazomethines (DPA) dendron encapsulated gold clusters having average cluster diameter of 2.2 nm.

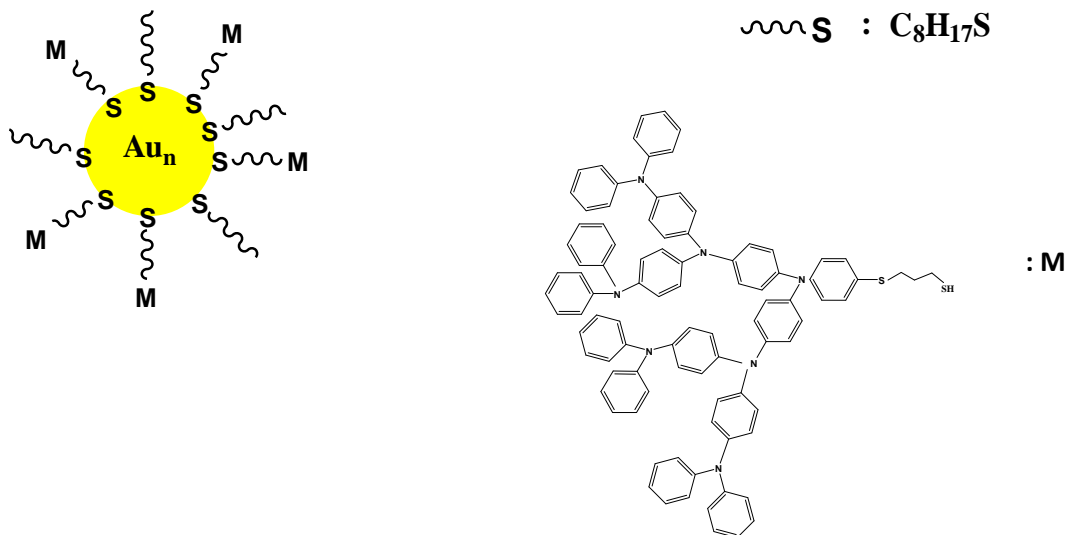


Fig 1. Gold clusters with DPA dendron

### Reverse micelle method

Reverse micelles are formed when surfactant molecules, possessing polar head group and hydrophobic tail, are placed in non-polar solvent. In reverse micelle structure surfactant molecules aggregate into nano sized spherical structures having core of polar head groups and shell of hydrophobic tails. If small amount of polar solvent is present in the mixture, it would be enclosed in core of reverse micelles. If this polar solvent contains an oxide precursor then controlled hydrolysis of precursor will be achieved by mixing small amount of water and small particles of metal oxide will form at core. Preparation of nano  $Al_2O_3$  by reverse micelle method is discussed below.

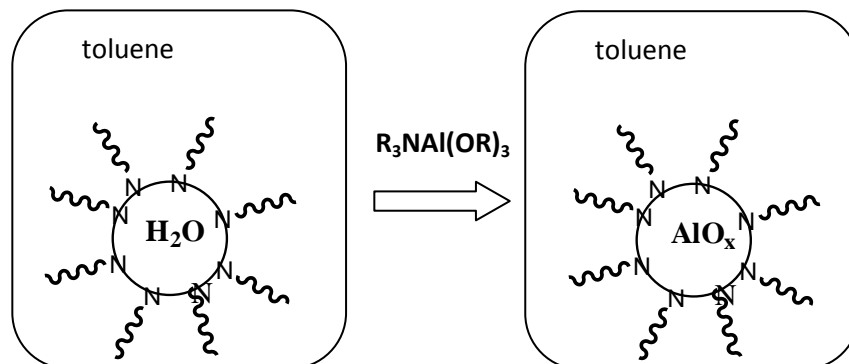


Fig 2. Schematics showing formation of nano-sized particles of aluminium hydroxide by reverse micelle method.



A solution of inverse micelles is first formed by adding a long chain alkylamine to a toluene solution. A small amount of water is trapped in the reverse micelle core. Mixing the reverse micelle solution with an aluminium alkoxo amine adduct results in hydrolysis of the aluminium alkoxide adduct and formation of nano-sized particles of aluminium hydroxide after drying.

Reverse micelle synthesis method is also reported for preparation of supported metal catalysts. Cheney et al. [5] reported synthesis of alumina supported Pt/Ni bimetallic catalysts by reverse micelle synthesis method. In this method two microemulsions were created by mixing 15% water, 10% surfactant and 75 % hydrocarbon( cyclohexane and propanol). Ni and Pt precursors were added to microemulsion -1 and hydrazine to the microemulsion -2. Each mixture was stirred separately for 1 h to allow micelles to equilibrate. In microemulsion-1 reverse micelles were formed having aqueous core and the Pt and Ni precursors were dissolved in aqueous polar core of the reverse micelles. Thereafter, the microemulsion –2 containing the reducing agent was added to the microemulsion -1 for insitu chemical reduction of the metals at reverse micelle core. The alumina support was added to the solution and titrated with acetone to disrupt the micelles and precipitate the nanoparticles onto the support. The supernatant was decanted and the catalyst powder was rinsed with acetone. Residual surfactant was removed by giving heat treatment in oxygen environment. By this method particles were obtained in the range of 1.4-2.8 nm.

## Application of nanocatalysts

### 1. Gold nanocatalysts

Supported gold nanoparticles have been reported to be very effective catalysts for oxidation of alcohols. Gold supported on graphite can oxidize glycerol to glycerate under relatively mild conditions. Under same conditions conventional supported Pt or Pd oxidation catalysts are much less selective.

### 2. Sulfated zirconia nanocatalysts

These catalysts are highly effective in refining processes replacing liquid acid catalysts. These are used in acid promoted catalytic reactions such as alkylation, dehydration, isomerization etc.

### 3. Dendrimer encapsulated nanoparticles (DENs)

Pd-DENs catalysts are studied as carbon-carbon coupling catalysts. In Heck coupling reaction, involving C-C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base, the Pd-DEN catalysts show higher activity and selectivity relative to other colloidal Pd catalysts.

### 4. Tungsten oxide and titanium oxide nanocatalysts

Tungsten oxide and titanium oxide due to their visible-ultraviolet band gap have been extensively studied in electro-catalytic and photocatalytic applications.

### 5. Transition metal or metal oxide nanoparticles

Transition metal or metal oxide nanoparticles have found important application in catalyzing growth of carbon nanotubes, carbon fibres, nanowires etc. Cobalt or cobalt oxide nanoparticles mixed with Ni is used in synthesis of single walled carbon nanotubes.

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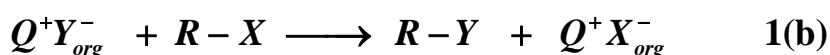
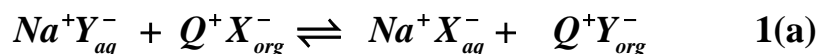
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## Lecture 41

### Phase Transfer Catalysis

Phase transfer catalysis (PTC) refers to reaction between two substances, located in different immiscible phases, in the presence of catalyst. Phase transfer catalysis is mainly used for synthesis of organics such as pharmaceuticals, dyes, chemicals etc. In this process one phase acts as a reservoir of reacting anions. The second phase, which is the organic phase, contains the organic reactants and catalysts generating lipophilic cations. The reacting anions enter the organic phase in ion pairs with lipophilic cations of the catalyst. Since the phases are mutually immiscible the reaction does not proceed unless the catalyst, usually a tetra alkyl ammonium salt,  $Q^+X^-$  is present. The catalyst transfers reacting anions into the organic phase in form of lipophilic ion-pairs produced according to the ion-exchange equilibrium (1a). In the organic phase the anions react such as in nucleophilic substitution as shown in 1(b) where alkyl halides undergo nucleophilic substitution. A variety of other reactions with participation of inorganic anions such as addition, reduction, oxidation, etc. can take place efficiently using this methodology.



The advantages of phase transfer catalysis can be summarized as :

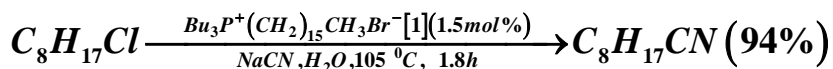
- Elimination of organic solvents
- Elimination of dangerous, inconvenient and expensive reactants
- high reactivity and selectivity of the active species
- high yields and purity of products
- simplicity of the procedure
- low investment cost
- low energy consumption
- minimization of industrial wastes
- mild reaction conditions

Suitable catalysts for PTC are those having highly lipophilic cation (that is cation having strong affinity for organics). The quaternary ammonium or phosphonium salts are most extensively used as phase transfer catalyst.

Examples of phase transfer catalyst are as follows:

- i. Tetra-alkyl-ammonium or phosphonium salts
  - Tetra-n-butyl ammonium bromide
  - Methyl-triethyl ammonium chloride
- ii. Tri-ethyl-benzyl-ammonium chloride

Displacement reaction of 1-chlorooctane with aqueous sodium cyanide is accelerated many thousand-fold by the addition of hexa-decyltributyl-phosphonium bromide as phase-transfer catalyst. Tremendous reactivity enhancement occurs due to generation of quaternary phosphonium cyanide, which makes cyanide anion organic soluble and sufficiently nucleophilic. In the absence of hexa-decyltributyl-phosphonium bromide phase transfer catalyst, no reaction occurs.



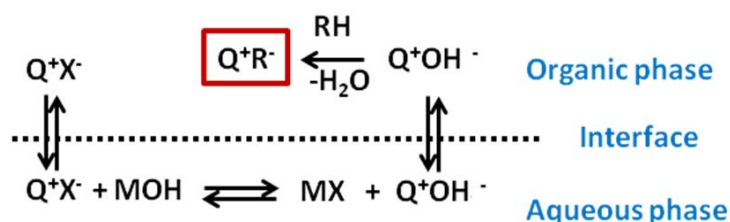
## Mechanism

Mechanistic aspects of phase-transfer catalysis remain obscure, mainly due to difficulty of investigating biphasic systems and the many complex parameters that must be analyzed. Two pathways are proposed

- i. Starks extraction mechanism
- ii. Makosza interfacial mechanism

### Starks extraction mechanism

According to this mechanism phase transfer catalyst moves back and forth across the organic and aqueous phases. The onium salt ( $Q^+X^-$ ) equilibrates with inorganic base (MOH) in aqueous phase, and extracts hydroxide into organic phase. Onium hydroxide ( $Q^+OH^-$ ) then abstracts hydrogen from the acidic organic compound to give the reactive intermediate  $Q^+R^-$ .



$Q^+X^-$  = tetra alkyl ammonium or phosphonium salts

**MOH** = inorganic base

Fig 1. Schematic diagram showing Starks extraction mechanism

### Makosza interfacial mechanism

There is initial formation of metal carbanion at interface in the absence of phase transfer catalyst. This is followed by extraction of metal carbanion species from the interface into the organic phase by action of phase-transfer catalyst. The mechanism is more plausible when phase-transfer catalysts are highly lipophilic and reluctant to enter aqueous phase.

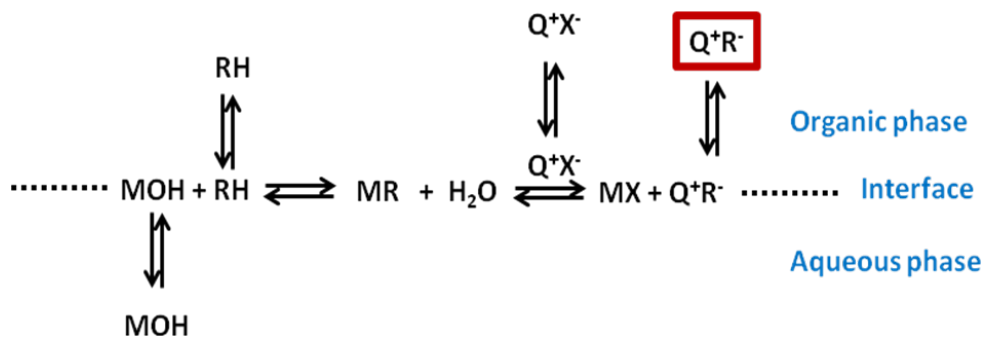


Fig 2. Schematic diagram showing Makosza interfacial mechanism

## Types of phase transfer catalysis

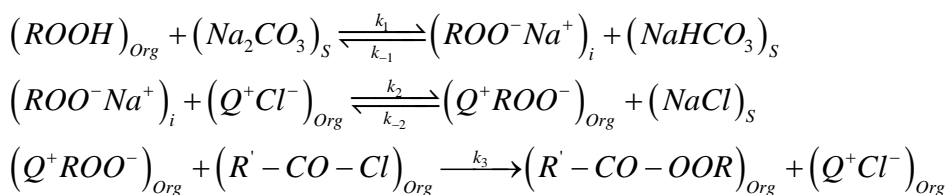
The phase transfer catalytic processes can be categorized as follows depending on the number of phases involved.

- i. liquid–liquid phase transfer catalysis
- ii. solid–liquid phase transfer catalysis
- iii. third-liquid phase-transfer catalysis

The liquid-liquid phase transfer catalysis has been discussed so far.

### Solid – liquid PTC

Solid liquid PTC is used for conducting a wide variety of organic transformations. The solid-liquid PTC usually involves reaction of an anionic reagent in a solid phase, with a reactant located in contiguous liquid organic phase. In solid-liquid PTC, the first step involves the transport of a reactant anion from the solid phase to the organic phase by a phase-transfer cation. The second step involves the reaction of the transferred anion with the reactant located in the organic phase. Solid – liquid PTC are used for alkylation of highly acidic compound, preparation of amino acids or aldol-type condensation. The process of hydroperoxide acylation in presence of anhydrous  $\text{Na}_2\text{CO}_3$  using solid – liquid PTC system can be demonstrated by a sequence of the following reactions as suggested by Baj et al. [1] :



The scheme is shown in Fig 3. A hydroperoxy anion is generated at the surface of solid  $\text{Na}_2\text{CO}_3$  which form a highly lipophilic ion pair  $[\text{ROO}^- \text{Q}^+]$  with the catalyst cation. This can be transferred deep into the organic phase where the specific reaction occurs producing the product.

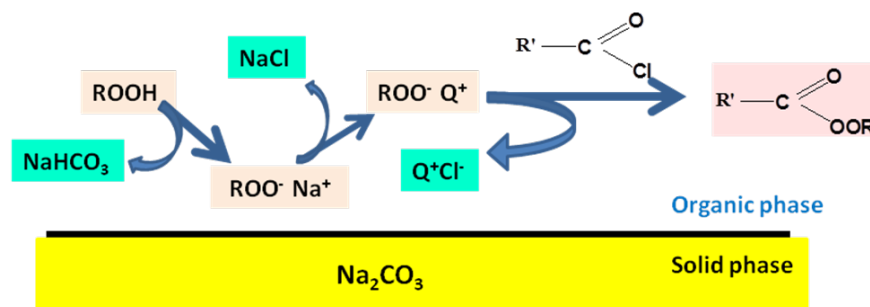


Fig 3. Schematic showing mechanism for acylation of hydroperoxides by acid chlorides in solid – liquid PTC

### Third-liquid phase transfer catalysis

In 1984, Neumann and Sasson investigated the isomerization of allylanisole using polyethylene glycol as catalyst in toluene and aqueous KOH solution and observed a third-liquid phase formed between the aqueous and organic phases. Third liquid phase is reported to be obtained at specified conditions :

- For phenethyl bromide to styrene using tetra-butyl-ammonium-bromide (TBAB) under phase-transfer conditions third-liquid phase only formed under conditions of using TBAB and 40% of aqueous NaOH solution.
- Solvents of different polarities and the amount of NaOH are two important factors in formation of third-liquid phase, the distribution of catalyst and the reaction rate



Advantages of third-liquid phase-transfer catalysis includes:

- higher reaction rates and selectivity
- easy separation of catalyst and product
- easy reuse and recovery of catalyst

Etherification reaction of aqueous sodium *o*-nitrophenoxide with 1-bromooctane can be carried out under third-liquid phase-transfer catalytic conditions. The reaction scheme shown in Fig 4 is proposed by Lin et al. [2].

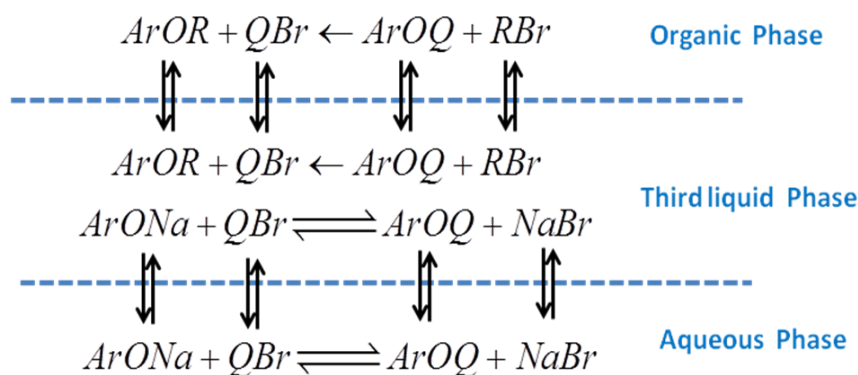


Fig 4. Schematic showing mechanism for etherification reaction of aqueous sodium *o*-nitrophenoxide with 1-bromo-octane in third-liquid phase transfer catalysis

## Industrial processes:

### Cyanation of alkyl chlorides

Cyanation of alkyl chlorides is a major way to produce nitriles. In the traditional process, since R-Cl and NaCN are mutually immiscible, solvents (lower alcohols-water mixtures) are used for reaction to proceed. In this process product has to be separated from the solvent and the solvent is reused. Another disadvantage is that the wastes, produced in substantial quantities, have to be destroyed and disposed.

In PTC methodology, neat alkyl chloride containing ~1% molar catalyst is stirred with saturated solution of NaCN in water. Upon completion of reaction in organic phase, which is often the pure product, is separated and product can be subsequently purified or used as such. Aqueous phase, after separation of solid NaCl, can be reused by introduction of fresh NaCN. Hence only waste in this method is solid NaCl.

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## Lecture 42

### Molecular modeling in heterogeneous catalysis

Heterogeneous catalytic cycles are complex process involving diffusion, adsorption, surface reaction and desorption. Further catalytic reactions involves individual phenomenon occurring on catalytic sites to overall reactions occurring in reactors which can be up to the size of 1 m diameter. Hence reactions can range in wide length scales. Relevant time scales can also span from femtoseconds ( $10^{-15}$ ) up to hours. This makes modeling of catalytic reactions challenging. Heterogeneous catalysis is traditionally considered as an experimental field and molecular modeling is emerging as complementary to experimental studies. Different computational methods at different time and length scales are co-linked to explain phenomenon from atomic to the macroscopic level. Computer modeling can provide new insights into reaction pathways and predict properties of catalysts. Modeling can be used to explain experimental results, suggest new experiments and substitute experiments in the screening of different catalysts or reaction conditions. Initially the modeling techniques need to be validated against experimental studies.

#### Different levels of molecular modeling

Molecular modeling needs to be carried out at different levels using different computational techniques. These models can then be correlated to obtain an overall view from atomic to macroscopic level. The different methods of molecular modeling include :

1. Quantum chemical calculations
2. Atomistic simulations
3. Microkinetic modeling

## 1. Quantum chemical calculations

Quantum chemical calculation method provides information about the smallest details in heterogeneous catalytic processes. Most detailed chemical informations are used to predict the energies, electronic structures, spectroscopic properties of small arrangements of atoms and catalytic chemistry. For example, activation energy barriers for individual elementary steps on surfaces can be calculated which is difficult to predict by experiments. Detailed information about presumed active sites for catalysis may be obtained because the explicit chemical details of system are considered. The method is based on solution of Schrödinger equation. Various methods have been advanced to solve the Schrödinger equation such as semi-empirical methods and ab-initio techniques.

### Semi-empirical methods

Semi-empirical methods are significantly less computationally demanding. This method introduces approximations to facilitate evaluation of terms introduced by electron – electron interactions. Method that has been most widely used for catalytic systems containing transition metals is ZINDO (Zerner's Intermediate Neglect of Differential Overlap). This semi-empirical method is extensively used to describe the electronic structure and the spectroscopic features of compounds [1]. It has also been used for understanding the reaction mechanism. Ma et al. [2] reported molecular simulation of the hydrodesulfurization mechanism of thiophenic compounds over molybdenum disulfide using ZINDO.

### Ab initio methods

These methods are more computational intensive. Among ab initio methods Hartree–Fock (HF) method adequately represent electron correlation such as configuration interaction and density functional theory (DFT). DFT calculations are reported more and more for various catalytic systems. Fajin et al. [3] used DFT to study the effect of doping of transition metals on gold catalyst for the reaction of oxygen dissociation. D'Amore et al. [4] investigated the adsorption of  $\text{TiCl}_4$  on the surfaces of  $\text{MgCl}_2$  crystals by DFT methods to study the structure of the active species in industrial  $\text{MgCl}_2$ -supported Ziegler–Natta catalyst used for ethene and propene polymerization.

## 2. Atomistic simulations

In addition to the events at the active site, physical adsorption and diffusion are important steps in a full catalytic cycle as discussed earlier. These phenomena which occur on longer time and length scales are analyzed using atomistic models. Atomistic simulations are used to predict macroscopic thermodynamic and transport properties such as adsorption isotherms, heats of sorption, diffusion coefficients and activation energies for diffusion. The method use systems of hundreds or thousands of molecules. Molecular simulation needs knowledge of the chemical composition and structure of the material. Basic structures can be determined by X-ray diffraction studies or other techniques. Simple potential functions describe the interaction energies between reactants and catalysts. Dispersion, repulsion, electrostatic forces and intramolecular forces are typically accounted. Induced dipole and other forces may also be included if they are considered to be important. Methods include Montecarlo and Molecular dynamics method.

## 3. Microkinetic modeling

Microkinetic modeling is used to link molecular-level informations about reactants, products and reactive intermediates on heterogeneous surfaces obtained by atomistic simulations and electronic structure calculations to macroscopic physical and chemical phenomena in systems involving chemical transformations. It is done using model parameters such as reaction rates, reactant conversion, product yields and selectivities predicted by the previous levels.

In this method no rate-determining mechanistic step (RDS) is assumed in contrast to more traditional models such as power law model or Langmuir–Hinshelwood–Hougen–Watson model. The mechanism for the reaction system is predicted based on experimental and theoretical study. All probable elementary steps are included. The rate constant for each of the elementary steps are specified from experiment or theory and the mechanism is then combined with the appropriate reactor design equations. The equations are solved to obtain relative reaction rates, coverage of surface intermediates, reactant conversion, product yields and selectivities. This is much more realistic method than traditional models where assumption of RDS is required. Non requirement of initial

assumption of RDS in this method is more accurate as the RDS can change with reaction conditions. However accurate parameters for all forward and reverse reactions are needed to solve the equations of the model. Thus result in requirement of huge amount of informations about interactions of chemical species with catalysts. This is one of the major disadvantages of microkinetic modeling and resulted in limitation of its usage. At present with simultaneous advances in spectroscopic, isotopic tracing and other experimental methods, obtaining detailed informations has become more feasible and consequently quantum chemical techniques and microkinetic models are being used more frequently.

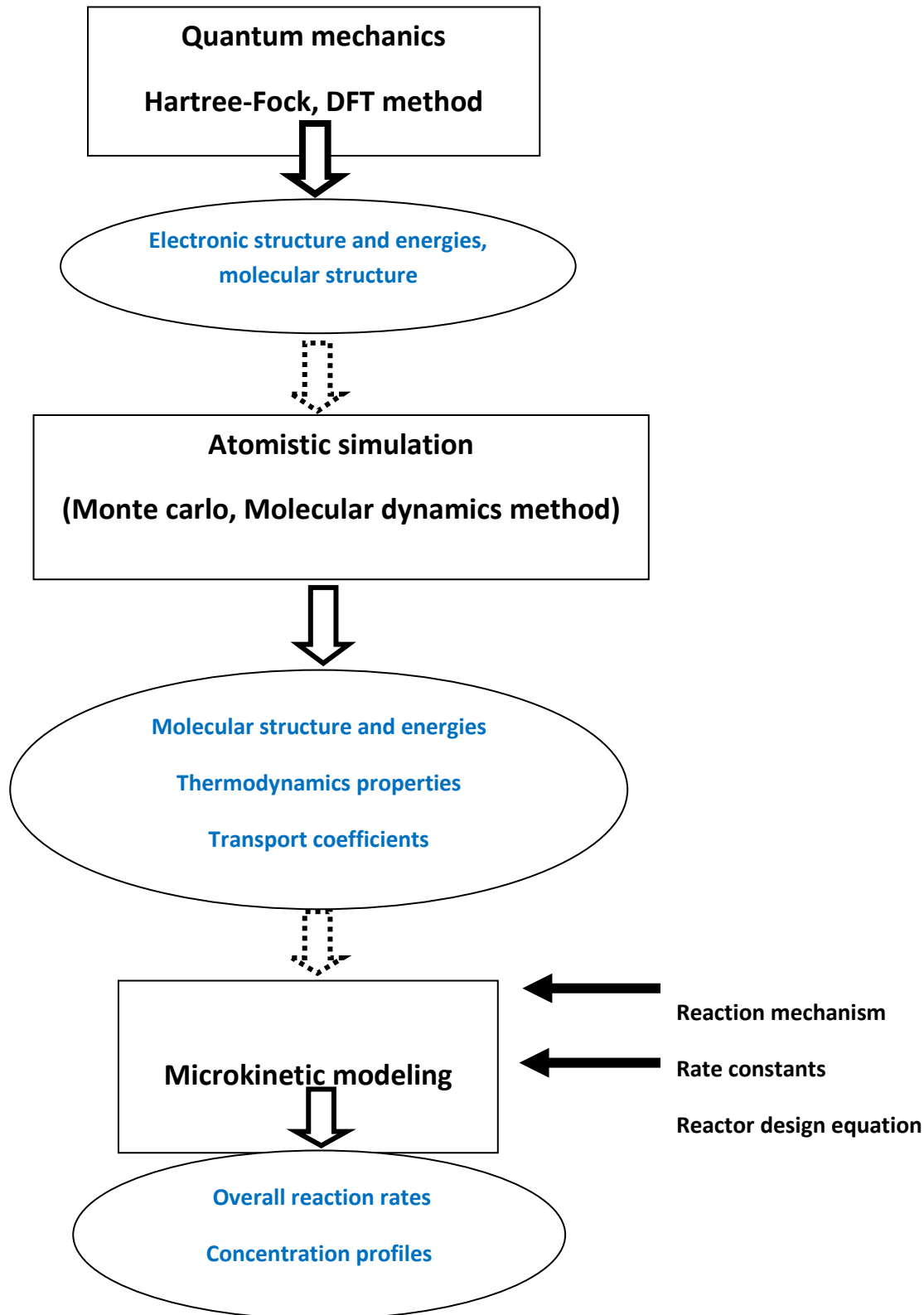


Fig 1. Flow diagram showing different levels of catalytic modeling

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