V SEMESTER

STUDY MATERIAL

COURSE – 7

GREEN CHEMISTRY AND NANO TECHNOLOGY

PREPARED BY

S. ANIL DEV

M. Sc.

LECTURER IN CHEMISTRY

D.N.R.COLLEGE (AUTONOMOUS) BHIMAVARAM

UNIT – I

GREEN CHEMISTRY PART – I

DEFINITIONS

Green chemistry is defined as environmentally benign chemical synthesis.

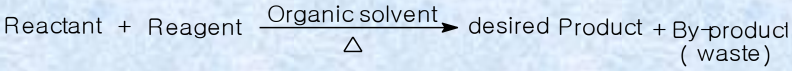
Or

It is the design of chemical products and processes are reducing or eliminating hazardous substances.

Or

It is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.

-- Anastas and Warner



$$\text{Reactant} + \text{Reagent} \xrightarrow[\Delta]{\text{Organic solvent}} \text{desired Product} + \underset{(\text{waste})}{\text{By-product}}$$

- Green chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feed stocks, products, by-products, solvent, reagents etc., those are hazardous.

Benefits of Green chemistry

- Economical
- Green chemistry method is more efficient than the conventional method.
- Green chemistry synthetic methods should have low energy requirements.
- Less wastes
- Fewer accidents protect human health and environment.

GOALS OF GREEN CHEMISTRY

The goal of green chemistry is the design of products and manufacturing processes to reduce their impact on human health and the environment. The green chemistry concept is the idea of sustainability reducing environmental impacts and conserving natural resources for future generation.

SOME OF THE GOALS OF GREEN CHEMISTRY

1. Sustainability

   Use renewable materials like garbage and biomass
2. Safety

   Prevention, less hazardous chemicals, reduced toxicity, safer solvents, minimizes accidents.
3. Process efficiency

   Atom economy, reduce derivatives, use catalysts, real-time analysis
4. Energy efficiency

   Design for energy efficiency
5. End of life degradation

   Design for degradation.
6. No chemical accidents

NEED FOR GREEN CHEMISTRY

1. Chemical developments also bring new environmental problems and harmful unexpected side effects, which result in the need for greener chemical products.
2. Green chemistry looks at pollution prevention on the molecular scale and is an extremely important area of chemistry due to the importance of chemistry in our world today and the implications it can show on our environment.
3. The green chemistry program supports the invention of more environmental friendly processes which reduce or even eliminate the generation of hazardous substances.
4. Green chemistry reduces toxicity, minimizes waste, and saves energy.

CONCEPT OF GREEN CHEMISTRY

1. Sustainable development
2. Atom efficiency
3. Solvent selection

The green chemistry concept is the idea of sustainability, reducing environmental impacts and conserving natural resources for future generation.

BASIC PRINCIPLES OF GREEN CHEMISTRY

Paul Anastas and John Warner proposed twelve principles for learning green chemistry.

1. Prevention of waste or by-products.

   Or

   It is better to prevent waste than to treat or cleanup waste after it is formed.
2. The final product should aim to contain all the atoms used in the process (Atom economy)

   Or

   Synthetic materials should be designed to maximize the incorporation of all materials used in the process into the final product.

   Ex: Traditional synthesis of ibuprofen → 6 stoichiometric stps -- < 40% AE

   Catalytic synthesis of ibuprofen → 3 stpes -- 80 % AE
3. Synthesis of less hazardous chemicals.

   Or

   Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

   Ex: Preparation of poly urethane from phosgene method

   Preparation of poly urethane from non-phosgene method (Green synthesis)
4. Designing of safer chemicals

   Or

   Chemical products should be designed to achieve their desired at the same time minimizing their toxicity.

   Ex: Acetanilide (toxic), paracetamol (less toxic)

5. Use of safer solvents and auxiliaries (Extra chemicals)

   Or

   The use of auxiliary substances (solvents or separation agents) should be made unnecessary whenever possible and when used, innocuous.

   Ex: water, supercritical CO_2, H_2O_2, Ionic liquids, poly ethylene glycol

6. Design for energy efficiency or Minimization of energy loss

   Or

   Energy requirement should be recognized for their environmental and economic impacts and should be minimized.

- If possible, synthetic methods should be conducted at ambient temperature and pressure.

  Ex: Microwave irradiation, sonication reaction or biological processes

7. Use of renewable feed stock

   Or

   A raw material or feed stock should be renewable rather than depleting, whenever technically and economically practicable.

   Ex: preparation of adipic acid from benzene (non-renewable)

   Preparation of adipic acid from glucose

8. Reduce derivatives

   Or

   Unnecessary derivatisation should be avoided whenever possible.

   Ex: Enzymatic reaction

9. Use of catalytic reagents

   Or

   Catalytic reagents are superior to stoichiometric reagents.

10. Design of environmental friendly and easily degradable products.

    Or

    Chemical products should be designed that at the end of their function they do not persist in the environment and breakdown into innocuous degradation products.

11. Real-time analysis for pollution and prevention

    Or

    Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.

- Analytical techniques are improved

12. Inherently safer chemistry for accident prevention

    Or

    Substances and the forms of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.

GREEN SYNTHESIS – EVALUATION OF THE TYPE OF THE REACTION

ATOM ECONOMY (A MEASURE OF EFFICIENCY OF REACTION) AND % OF ATOM UTILIZATION.

Atom economy gives the number of atoms of reactants and reagents converted in desired product and by-product (waste)

$$\textbf{\% of atom economy} = \frac{\textit{Formula weight of desired products}}{\textit{Formula weight of all reactants}} \textbf{ X 100}$$

If the % of atom economy is 100%, the reaction comes under green synthesis.

Ex:1 AE of CO_2

$$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$$

$$\text{Desired product} \longrightarrow 3(12 + 2 \times 16) = 132$$

$$\text{Reactants} \longrightarrow 3 \times 12 + 8 \times 1 + 5(2 \times 16) = 204$$

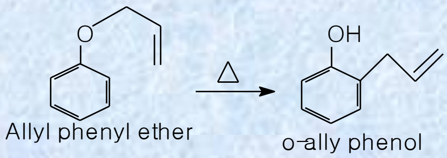
$$\text{\% of atom economy} = \frac{132}{204} \text{ X } 100$$

$$= 64.6\%$$

i) REARRANGEMENT REACTIONS (100% ATOM ECONOMY)

In rearrangement reactions all atoms of reactants are utilizing in the product % of atom economy is 100% and it comes under green chemistry.

Ex: AE of o-allyl phenol



Reactant $C_9H_{10}O \longrightarrow 134$

Product $C_9H_{10}O \longrightarrow 134$

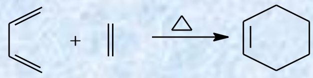
$$\% \text{ of atom economy} = \frac{134}{134} \times 100$$

$$= 100\% \text{ Green synthesis}$$

ii) ADDITION REACTIONS (100 % ATOM ECONOMY)

In the addition reactions all the reagent atoms added to the reactant molecules. These reactions are 100 % atom economy processes.

Ex: Diels-Alder reaction: (4 + 2) cyclo addition reaction



$$\% \text{ of atom economy} = \frac{82}{82} \times 100 \quad = 100\% \text{ Green synthesis}$$

% OF ATOM UTILIZATION

According to B M Trost we must find out that how many atoms that are found in the reactants are incorporated into the final product. From this we can find out the formation of waste by-products if any.

% of atom utilization =

$$\frac{\textit{Molecular weight of desired products}}{\textit{Molecular weight of desired products} + \textit{Molecuar weight of waste product}} \times 100$$

GREEN SYNTHESIS

Environmentally benign chemical synthesis

Or

It is an environmental friendly method presenting a different way of thinking in chemistry intended to eliminate toxic waste, reduce energy consumption and to use ecological solvents (water, ethanol and ethyl acetate)

METHODS OF GREEN SYNTHESIS

1. Microwave irradiation
2. Hydrothermal synthesis
3. Ultra sound-assisted (sono chemical) synthesis
4. Solvents and catalysis in green processes

Advantages of green synthesis

It is cost-effective, non-toxic, robust and easy to manage.

SONO CHEMISTRY

It is the study of effects of ultra sound on chemical activity of a reaction mixture. Use of ultrasound in organic synthesis is called sonification and the subject is called sono chemistry.

SONICATION

The processes of applying sound energy for agitate particles or discontinuous fibers in a liquid. Ultra sonic frequencies (> 20 kHz) are usually used. So the process is also known as Ultra sonication.

ULTRA SOUND

Any sound of frequency above that to which the human ear has no response.

Ultrasound is represented by the symbol **)))))**

SONICATION REACTIONS

The chemical reactions takes place in presence of ultra sound may be environmentally benign. The type of ultra sound used is power ultra sound (frequency between 20 – 100 kHz). These reactions are also known as sonication reactions.

Most of the sono chemical reactions are conducted in solution. The instrument for the generation of ultrasound consists of an ultrasonic transducer (electrical or mechanical energy is converted to sound energy)

Apparatus

In the laboratory, it is usually applied using an ultrasonic bath or an ultrasonic probe / horn, colloquially known as sonicator. In a paper machine, an ultrasonic foil can distribute cellulose fibers more uniformly and strengthen the paper. Sonicators are high frequency sound generators used to disrupt cells or shear nucleic acids.

BASIC PRINCIPLE OF SONICATOR

When low pressure is applied to the liquid, high intensity ultrasonic waves are produced, creating small vacuum bubbles in the liquid. As the bubbles reach their saturation level, they collapse and this happens in the high pressure cycle.

Or

The interaction pressure waves (ultrasound) with a liquid medium leads to the formation of cavities in liquid.

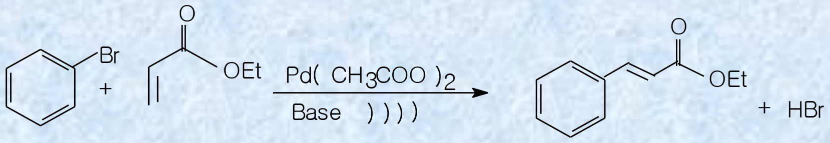
ADVANTAGES OF SONICATION METHOD

1. It is clean, economical, efficient and safe procedure.
2. This can lead save time, energy and money.
3. Very rapid reactions, frequently in few minutes.
4. Higher degree of purity achieved.
5. Workup procedure is very simple.

Examples

1. **HECK REACTION**

   The coupling of aryl halides with alkenes in the presence of palladium catalyst.



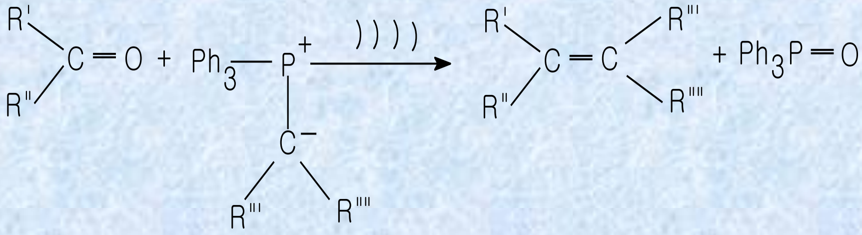
2. **HUNDSDIECKER REACTION**

   In this reaction silver salts of carboxylic acids react with a halogen to produce an alkyl halide.

$$RCOOAg + Br_2 \xrightarrow[))))]{} R-Br + CO_2 + AgBr$$

3. **WITTIG REACTION**

   In this reaction an aldehyde or ketone reacts with a triphenyl phosphonium ylide (wittig reagent) to give an alkene and triphenyl phosphine oxide.



UNIT – II

GREEN CHEMISTRY PART – II

A) SELECTION OF SOLVENT

The solvent selected for a particular reaction should not have any environmental pollution and health hazard. Green chemistry suggests the use of alternative solvents. Some common alternate solvents are water, super critical fluids like carbon dioxide, ionic liquids, solvent free processes and bio-solvents.

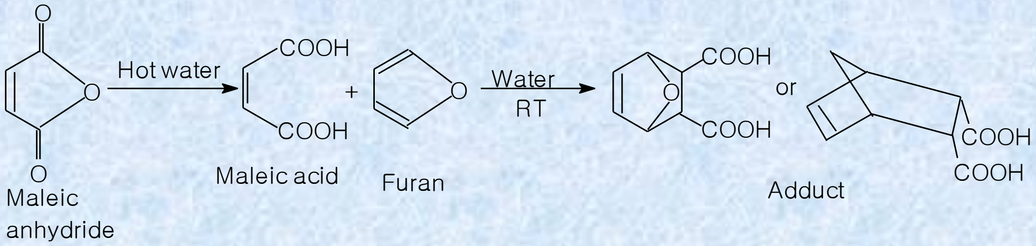
i) AQUEOUS PHASE REACTIONS

Organic reactions carried in aqueous phase i.e. using water as solvent are known as aqueous phase reactions. Water is always a preferred solvent, it causes no environmental pollution and is never a health hazard to human beings working with it. Using water as a solvent offers many advantages such as low cost, non-inflammable, non-carcinogenic and simple operation.

Example

DIELS-ALDER REACTION

In hot water maleic anhydride is hydrolyzed into maleic acid. The reaction between furan (diene) and maleic acid(dienophile) in water at room temperature to give an adduct furn-maleic acid.



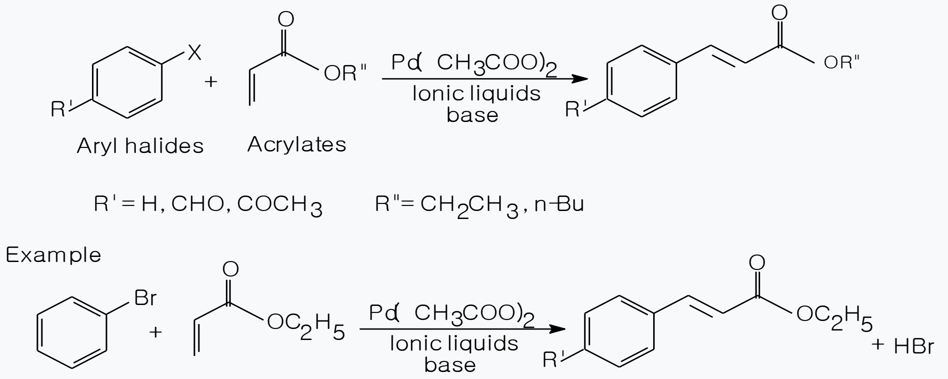
ii) REACTIONS IN IONIC LIQUIDS

Ionic liquids are made up of at least two components in which the cation and anion can be varied. The ionic liquids are immiscible in water. By cooling the correct ionic liquids, higher product yield can be obtained and a reduced amount of waste is produced in a given reaction with the elimination of solvents. Ionic liquids are good solvents for a wide range of both inorganic and organic materials.

Examples

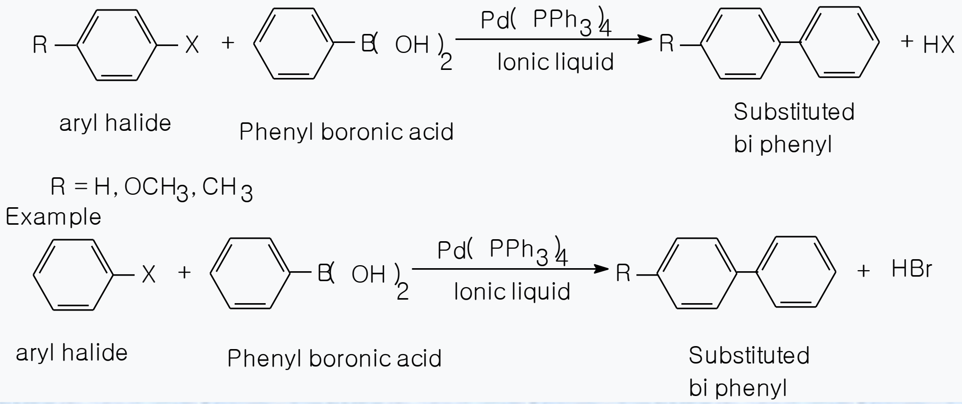
HECK REACTION

Heck coupling of aryl halides with alkenes in the presence of palladium catalyst. This reaction carried out in ionic liquids at room temperature.



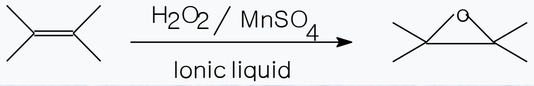
SUZUKI REACTION

It is a coupling reaction. In the presence of palladium salt aryl halides are react with phenyl boronic acid to give substituted biphenyl.



EPOXIDATION

Conversion of unsaturated compound into an epoxide. Epoxidation of alkene using hydrogen peroxide was achieved with manganese sulfate or bicarbonate in an ionic liquid.



iii) SOLID SUPPORTED SYNTHESIS

Organic synthesis in solid state is mostly green reactions. These are of two types.

a) Solid supported organic synthesis
b) Solid phase organic synthesis without any solvent

SOLID SUPPORTED ORGANIC SYNTHESIS OR SOLVENT FREE REACTIONS OR SOLID STATE REACTIONS

In these reactions, the reactants are taken in a suitable solvent like water, alcohol, methyl chloride etc. with a suitable adsorbent or solid support like silica gel, alumina etc. is added. The contents are thoroughly stirred and the solvent is removed. The dried solid supports on which the reactants have been adsorbed are used for carrying out the reaction under microwave irradiation. These reactions are also known as solvent-free reactions.

In the microwave solvent free reactions the excess energy in the reaction medium is absorbed by solid support. The decomposition of the product is minimized. Solid supports increase the purity of the products.

SUPER CRITICAL FLUIDS

A substance held at or above its critical pressure and temperature.

Or

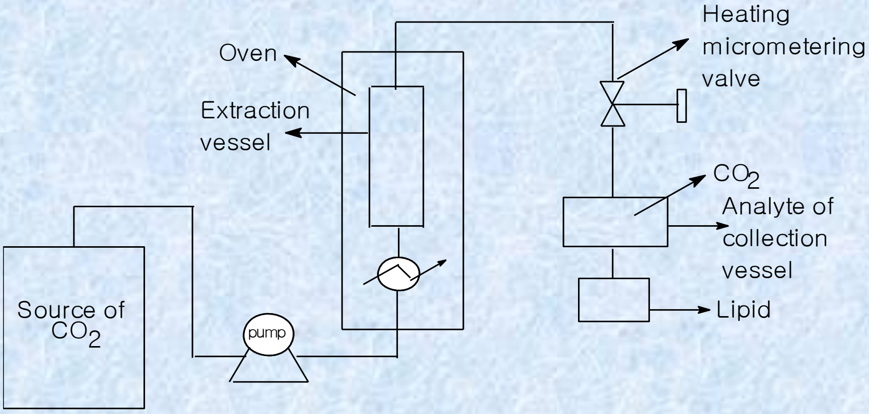
It is a material that can be either liquid or gas used in a state above the critical temperature and the critical pressure where gases and liquids can coexist.

B) Super critical carbon dioxide

Super critical carbon dioxide is a liquid state of carbon dioxide (at 31^0C, 73 atm). Carbon dioxide usually behaves as a gas in air at STP or as a solid called dry ice when frozen. If dry ice is put in an enclosed vessel, it will sublimate to become a gas and the pressure will increase depending on the mass of dry ice until the desired pressure (super critical pressure) is achieved.

Properties

It is non-toxic, non-flammable, renewable, and very low cost and leaves no residual solvents.



Critical extraction method

APPLICATION OF SUPER CRITICAL CARBON DIOXIDE

It has been widely used in the food and pharmaceutical industries for extraction.

1. DE CAFFEINATION

Coffee is one of the most popular beverages in the world. The caffeine content of green coffee beans contains about 1.0 to 2.0 %.

Decaffeination processes are two types

1. Solvent based or organic process
   a) The direct or natural decaffeination method
   b) The indirect or water processed method
2. Non-solvent or inorganic process

   This process is done without the use of any solvent. It is further divided into two methods.

   a) The Swiss water decaffenation method
   b) Super critical carbon dioxide method.

SUPER CRITICAL CARBON DIOXIDE METHOD

In this method coffee seeds are soaked in water and are transferred to a high pressure stainless steel vessel called the extraction vessel. The vessel is sealed and liquid carbon dioxide is forced in to the coffee seeds at high pressure of about 1000 pounds / square inch. This removes caffeine leaving behind the coffee seeds and its other constituents. The caffeine lead carbon dioxide is transferred to another container called the absorption vessel. The pressure is released converting the liquid carbon dioxide to its gaseous state. This gaseous carbon dioxide is drain out from the container for future use. This method is expensive.

HEALTH BENEFITS OF DECAFFEINATED COFFEE

a. Decaffeinated coffee reduces the risk of type-2 diabates.
b. It has a positive effect on aging and reduces the risk of neuro degenerative diseases like Parkinson’s disease.
c. It reduces the symptoms of heart burn.

3. DRY CLEANING

Super critical carbon dioxide can be used as a more environmental friendly solvent for dry cleaning over traditional solvents such as hydro carbons. Green dry cleaning refers to any alternative dry cleaning method that does not involve using PERC(per chloro ethylene). One is wet cleaning which is a more gentle version of home laundering. Three other cleaning methods follow the traditional solvent model but use carbon di oxide, hydro carbon or silicon based cleaners instead of PERC. However, only two are considered truly safe for the environment and consumers. They are wet cleaning and liquid carbon di oxide cleaning. Liquid carbon dioxide is non-toxic and is actually used to provide carbonation to soft drinks.

C) GREEN ENERGY

It is any energy type that is generated from natural resources, such as sunlight, wind or water.

Ex: solar energy, wind energy, hydro energy, tidal energy, bio mass energy.

SUSTAINABILITY

Meet our own needs without compromising the ability of future generations to meet their own needs. Or

Using of products or services in a way that does not damage the future generation resources. Hence, while a final product may be green, its manufacturing or production process may not be sustainable at all. Sustainability improves the quality of our lives, protects our ecosystem and preserves natural resources for future generations. Human, social, economic and environmental are four pillars of sustainability.

Ex: Renewable energy such as solar, wind.

UNIT – III

MICROWAVE AND ULTRASOUND ASSISTED GREEN SYNTHESIS

MICRO WAVE ASSISTED ORGANIC SYNTHESIS (MAOS)

Microwave induced organic reaction enhancement (MORE) chemistry reactions are extremely fast, cleaner than conventional reactions and lead to higher atom economy (less chemical waste). Microwaves have the wavelength 10 cm – 1 m (30 GHz – 300 Hz). Microwave are used for heating purpose it involves selective absorption of radiation by polar molecules to convert into product, the non-polar molecules being inert to microwave radiation.

Under microwave conditions reactants convert into products with in short period (sec – min) when compared to classical heating condition. The yield of the product under microwave conditions is high, when compared to the classical method, because under conventional heating the product formed may be some time decomposed and decreases its yield. But under microwave irradiation there is no decomposition of the product because the reactions are carried out under appropriate frequency at a particular time. In the microwave heating the energy is directly absorbed by the molecules through their bonds. The breaking and making of bonds during the reaction become rapid and the reactions are completed in a short time.

ADVANTAGES OF MAOS

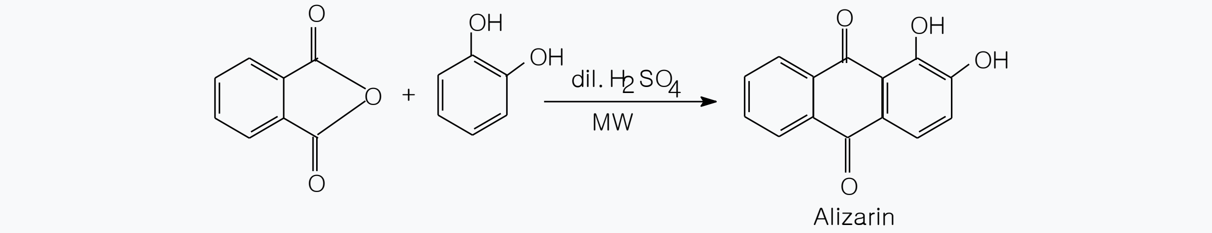
1. It is clean, economical. Efficient and safe procedure.
2. This can lead to save time and money
3. Very rapid reactions, frequently in few minutes.
4. Higher degree of purity achieved
5. Workup procedure is very simple
6. Some reactions may be possible without solvent
7. Most advantages of MW condition is the reactions may be possible in the solid state

DIS ADVANTAGES OF MAOS

1. MW assisted technology is not applicable to all the reactions i.e. less polar and non-polar reactants do not react under MW conditions.
2. MW assisted technology is not applicable to study the reaction kinetics, rate of reaction and the intermediate formation.
3. MW technology is useful to carry out the reaction with a reactants in small volume
4. Excess supply of MW energy may lead to explosion.

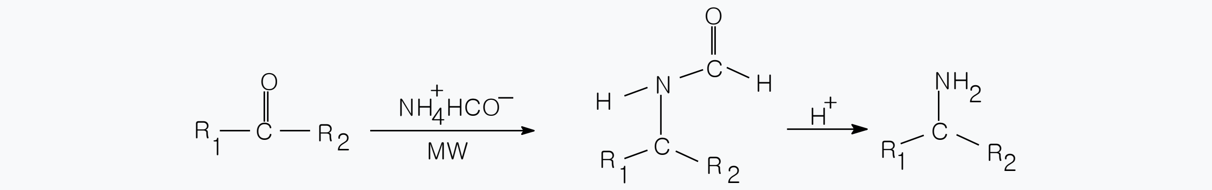
1. SYNTHESIS OF FUSED ANTHRAQUINONE

A mixture of phthalic anhydride, catechol in presence of dil. H_2SO_4 irradiated in microwave to get alizarin (anthraquinone compound)



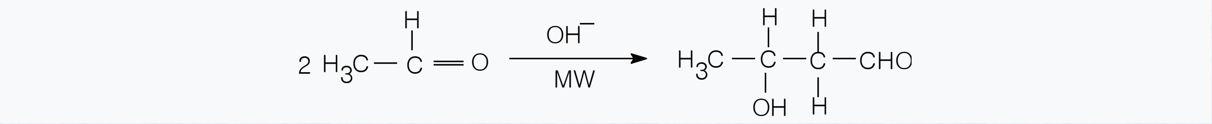
2. LEUKART REDUCTIVE AMINATION OF KETONES

Leukart reaction converts ketones to amines by reductive amination under microwave condition.



3. ALDOL CONDENSATION

Under the influence of dilute base or dilute acid two molecules of an aldehyde or a ketone with α-hydrogens may combine to form β-hydroxy aldehyde or β-hydroxy ketone.

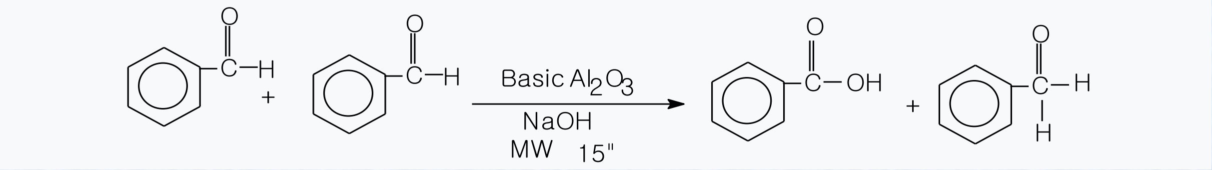


4. CANNIZAARO REACTION

The microwave assisted cannizaro reactionwas studied in order to develop fully reproducible synthetic protocols for transformation of aldehydes to carboxylic acid and alcohol.

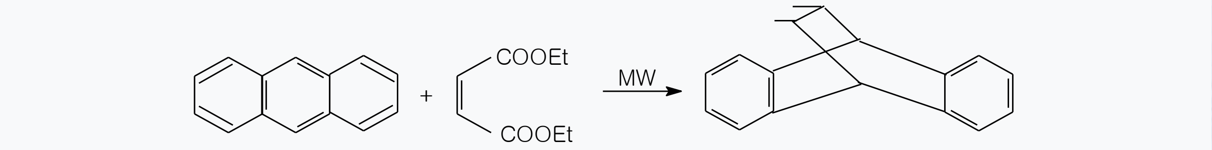
Or

In the presence of concentrated alkali, aldehydes containing no α-hydrogens undergo (disproportion) self-oxidation and reduction to yield a mixture of an alcohol and carboxylic acid.



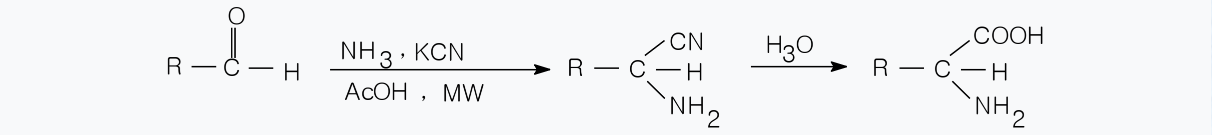
5. Diels alder reaction

In the presence of microwave conjugated diene and a substituted alkene(dienophile) react to form a Diels-Alder adduct.



6. Strecker synthesis

Aldehydes react with a mixture of KCN, ammonia and acetic acid to give amino nitrile which on hydrolysis gives α-amino acids.



UNIT – IV

GREEN CATALYSIS AND GREEN SYNTHESIS

GREEN CATALYSIS

Conversion of stoichiometric processes to homogeneous and heterogeneous catalytic reactions by using organic, organo metallic, inorganic and biological catalysts.

CATALYSIS

It is a fundamental pillar of green chemistry. It is the 9th and one of the most important principles of green chemistry.

“Catalysis refers to changing the speed of reaction using a substance that’s not consumed by the reaction”

Or

Catalysis is a term describing a process in which the rate of the reaction is influenced by the presence of a substance (catalyst) that is not consumed during the reaction and that is subsequently removed if it is not to constitute as an impurity in the final product.

TYPES OF CATALYSIS

1. Homogeneous catalysis
2. Heterogeneous catalysis
3. Auto catalysis

HETEROGENEOUS CATALYSIS

It is catalysis where the phase of catalysts differs from that of the reactants or products.

ZEOLITES

Any of a large group of minerals consisting of hydrated alumino silicates of sodium. Potassium, calcium and barium. They cn be readily dehydrated and rehydrated and are used as cation exchanges and molecular sieves. Zeolites are micro porous, three dimensional crystalline solids of aluminium silicate.

USE OF ZEOLITES

There are three main uses of zeolites in industry. Catalysis, gas separation and ion-exchange. Zeolites are extremely useful as catalysts for several important reactions involving organic molecules. The most important are cracking, isomerization and hydro carbon synthesis. Zeolites can be used to remove the hardness of water. When the hard water sample is made to pass through zeolite channels the calcium and magnesium ions get replaced by sodium ions.

SILICA (SIO_2)

Silica and silicon nano materials have diverse applications in the field of drug / gene delivery, light weight aggregates, regenerative medicine, tissue engineering, cancer diagnosis / therapy, catalytic applications and energy storage.

ALUMINA (ALUMINIUM OXIDE AL_2O_3)

Alumina is used to absorb impurities in the organic synthesis field and as a stationary phase substance in chromatography.

BIO CATALYSIS

The use of natural catalyst such as proteins and enzymes are performing transformation of organic compounds.

Or

Bio catalysis refers to the use of living systems or their parts to speed up chemical reactions.

Or

The use of natural substances includes enzymes from the biological sources or whole cells to speed up chemical reactions.

All the reactions that take place in the biological systems are enzyme catalyzed i.e. bio catalyzed. Each biological reaction is catalyzed by a specific enzyme. Enzyme can increase the rate of reaction.

Ex:1. Baker’s yeast releases the enzymes invertage and zymase.

7. Vitamin B is the thiamine hydrochloride a co-enzyme.

MICROBES

These are tiny living things that are found all around us and are too small to be seen by the naked eye. They live in water, soil and in the air. The human body is home to millions of these microbes. These are also called as microorganisms. Some microbes make us sick, others are important for our health.

Ex: microscopic fungi, protozoa, algae, bacteria.

PHASE TRANSFER CATALYSIS

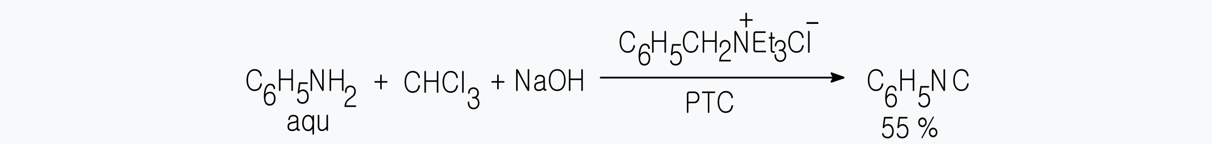
Substance which helps in the transfer of one of the reactant from one phase to another are called phase transfer catalysts and phenomenon is called phase transfer catalysis.

Ex: Quaternary ammonium salts, phosphonium salts, crown ethers

Example 1

PREPARATION OF PHENYL ISOCYANIDE

It is prepared by the reaction of di chloro benzene by the PTC method from aniline.



$$\underset{\text{aqu}}{C_6H_5NH_2} + CHCl_3 + NaOH \xrightarrow[\text{PTC}]{C_6H_5CH_2\overset{+}{N}Et_3\overset{-}{Cl}} \underset{55\ \%}{C_6H_5NC}$$

PROCEDURE

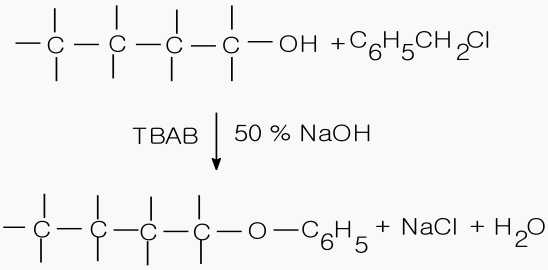
To the mixture of aniline, chloroform and benzyl tri ethyl ammonium chloride, add a vigorously stirred solution of NaOH. The reaction subsides in 4 – 5 minutes and the stirring is continued for one hour. After the reaction is over, add cold water. Extract the mixture with methylene chloride, wash the organic layer with aqueous NaCl and dry over anhydrous sodium sulphate, distil the clear solution under nitrogen phenyl isocyanide is collected at 50 – 52 ^{0}C/11 mm. yield is 57%.

The usual method of preparation of phenyl isocyanide without the PTC gives very poor yield i.e. 5 – 10%.

Example 2

Preparation of n-butyl benzyl ether

It is obtained by an improved Williamson ether synthesis using PTC. The reaction of butyl alcohol with benzyl chloride in presence of sodium hydroxide and tetra butyl ammonium bi sulphate (TBAB) as catalyst gives n-butyl benzyl ether.



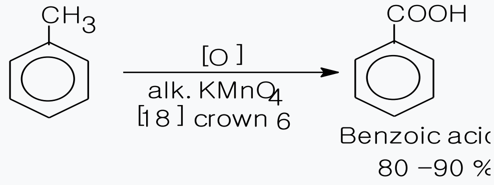
PROCEDURE

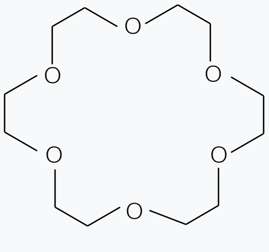
A mixture of n-butyl alcohol, benzyl chloride, sodium hydroxide solution and TBAB is stirred at 35 – 40^{0}C for 1.5Hr. Extract the mixture with THF, sash THF solution with sodium chloride saturated with 50% aqueous sodium hydroxide. Distillation of the dried THF solution gives the required n-butyl benzyl ether in 92% yield.

Example 3

OXIDATION OF TOLUENE TO BENZOIC ACID

Normally toluene is oxidized to benzoic acid by alkaline KMnO4 solution. However even after prolonged refluxing, the yield is only 40 – 50 %. Use of PTC or crown ether ([18] crown 6) gives much better yield 80 – 90 % in shorter time.





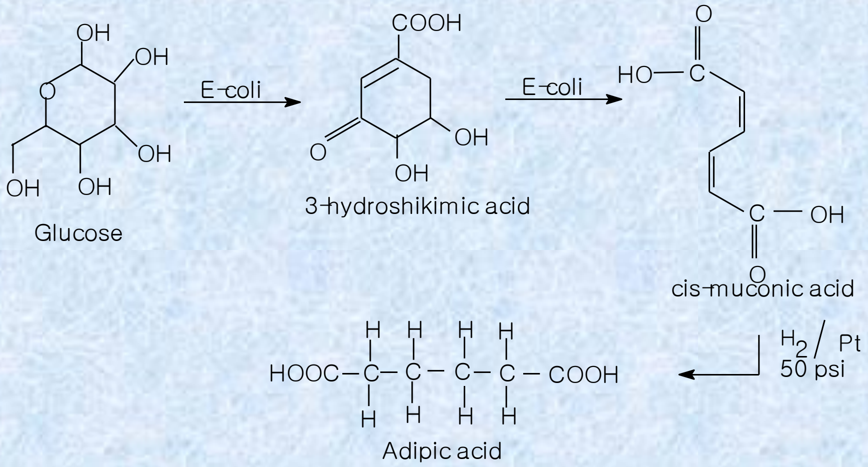
18-crown-6

NAME OF THE FACULTY: ***S. ANIL DEV***
LECTURER IN CHEMISTRY
D.N.R.COLLEGE (A), BHIMAVARAM

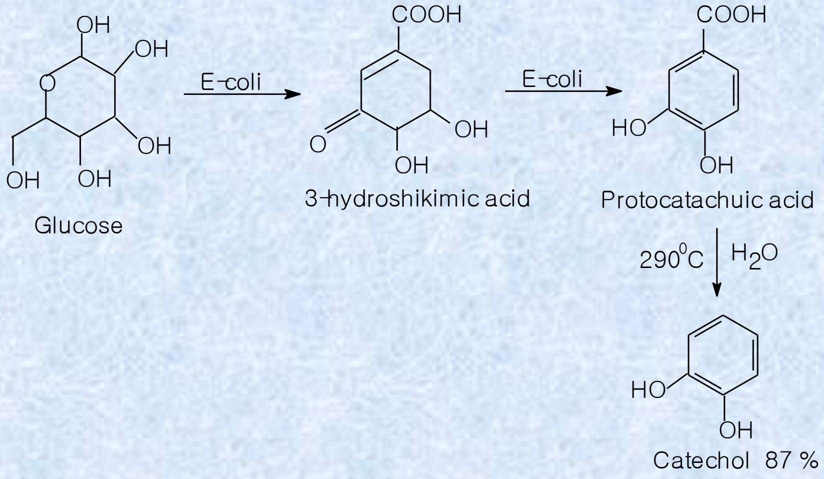
GREEN SYNTHESIS

1. SYNTHESIS OF ADIPIC ACID FROM GLUCOSE

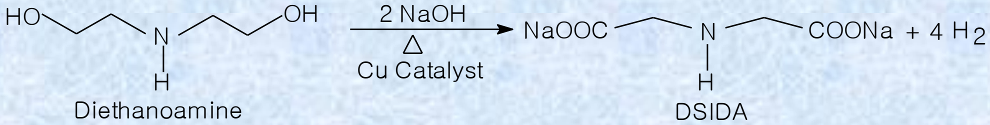
An environmentally benign (or green) synthesis of adipic acid was developed by John W Forst and Kaven M Draths, starting with glucose. In this reaction a bio catalyst i.e. genetically altered E-coli bacteria is used. The environmentally benign synthesis of adipic acid uses D-glucose (non-toxic, renewable source) and the starting material. Also the synthesis is conducted in water instead of organic solvents.



2. SYNTHESIS OF CATECHOL



3. SYNTHESIS OF DI SODIUM IMINODIACETATE (DSIDA) ALTERNATIVE TO STRECKER SYNTHESIS



MICRO WAVE ASSISTED REACTION IN WATER

Due to the ability of some compounds (solids or liquids) to transform electromagnetic energy into heat. MW radiation has been widely employed in chemistry as an energy source.

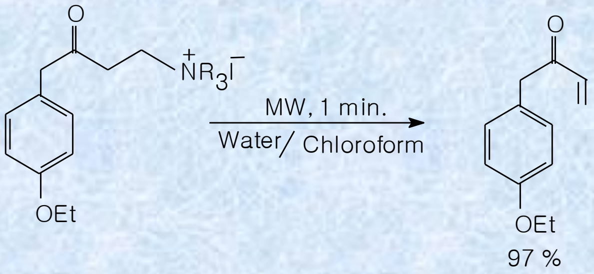
MW energy is non-ionizing and thus does not change the molecular structure of the compounds, it provides thermal activation.

Micro waves are present in between infrared and radio waves.

Water as a solvent is not only in expensive and environmentally benign but also shows completely different reactivity to organic solvents.

1. HOFFMANN ELIMINATION

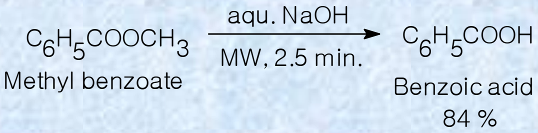
Normally quaternary ammonium salts are heated at high temperature and the yield is low. Use of MW irradiation gives much better yield.



2. HYDROLYSIS OF METHYL BENZOATE TO BENZOIC ACID (SAPONIFICATION)

Saponification of methyl benzoate in aqueous NaOH under MW condition (2.5 min.) gives 84 % yield of benzoic acid.

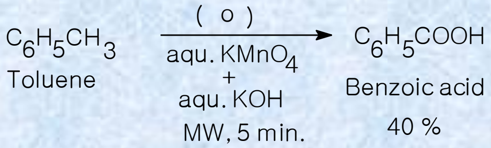
In presence of an acid under MW Hydrolysis of methyl benzoate to benzoic acid



$$\underset{\text{Methyl benzoate}}{C_6H_5COOCH_3} \xrightarrow[\text{MW, 2.5 min.}]{\text{aqu. NaOH}} \underset{\text{Benzoic acid}\ 84\ \%}{C_6H_5COOH}$$

3. OXIDATION OF TOLUENE

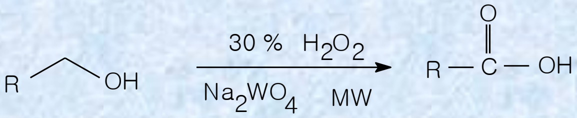
Oxidation of toluene to benzoic acid with aqueous $KMnO_4$ in the presence of aqueous KOH under MW irradiation.



$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[\text{aqu. } KMnO_4 \text{ + aqu. KOH, MW, 5 min.}]{(o)} \underset{\text{Benzoic acid 40 \%}}{C_6H_5COOH}$$

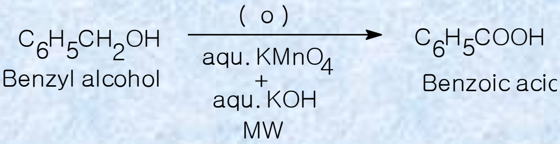
4. OXIDATION OF ALCOHOL

Primary alcohols can be oxidized to carboxylic acid using sodium tungstate as a catalyst in presence of 30 % aqueous hydrogen peroxide under MW irradiation.



$$R-CH_2-OH \xrightarrow[Na_2WO_4 \quad MW]{30\ \%\ H_2O_2} R-\overset{\overset{O}{\|}}{C}-OH$$

Oxidation of benzyl alcohol to benzoic acid with aqueous $KMnO_4$ in presence of aqueous KOH under MW irradiation



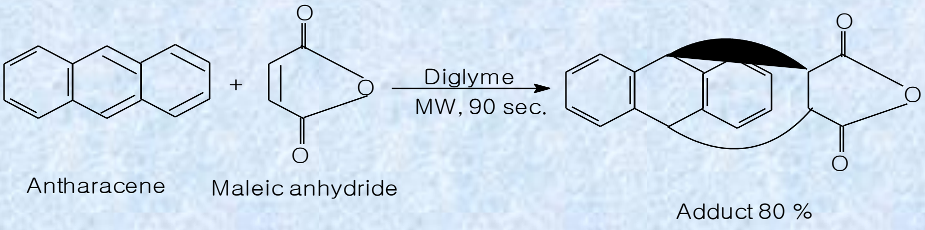
$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \xrightarrow[\text{aqu. } KMnO_4 \text{ + aqu. KOH, MW}]{(o)} \underset{\text{Benzoic acic}}{C_6H_5COOH}$$

MICROWAVE ASSISTED REACTION INORGANIC SOLVENTS.

Organic solvents are known as carbon based solvents. Solvent should be used as polar because non-polar solvents are inert to MW radiation. The most widely used organic solvent for MWI is DMF (N,N-dimethyl formamide) with high dielectric constant (2.2 to 2.7), it increases the MW absorption. Some other organic solvents are formamide, chloro benzene, 1,2,3-trichloro benzene, ethylene glycol.

Ex: **Diels-Alder reaction**

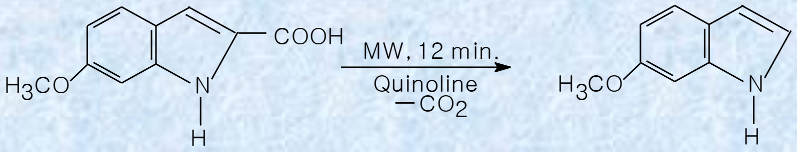
1,4-addition of an alkene to a conjugated diene to form an adduct under MW conditions diglyme is used as solvent. 80 % yield of adduct is obtained in one minute.



Ex: **Decarboxylation reaction**

Conventional method of decarboxylation of carboxylic acids needs refluxing in quinolone as a solvent and copper chromate as catalyst with low yields. In MW decarboxylation reaction takes place in shorter time with high yield (99 %)

It is a chemical reaction that removes carboxyl group and releases carbon di oxide.



6-methoxyindole-2-carboxylicacid

6-methylindole
99 %

ULTRA SOUND ASSISTED REACTIONS

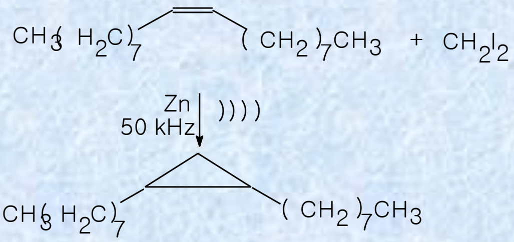
The chemical reactions takes place in presence of ultra sound may be environmentally benign. The type of US used is power US (frequency between 20 – 100 kHz). These reactions are also known as sonication reactions.

SIMMON – SMITH REACTION

In these reactions, to clean the metal surface, iodine is used. US act as an alternative to iodine effectively. Reactions run gently and give high yields.

The simmon-Smith reaction involving an organo zinc carbenoid that reacts with an alkene to form a cyclo propane.

Zn/CH_2I_2 is known as Simmon-Smith reagent.



UNIT – V

NANOTECHNOLOGY IN GREEN CHEMISTRY

If the particles sizes are in 1 – 100 nm ranges, they are generally called Nano particles or materials.

Or

The materials of at least one dimension between 1 nm to 100 nm are known as Nano materials.

1 nm= 10^{-9} m

It is an advanced technology which deals with the synthesis of Nano particles, processing of the Nano materials and their applications. Nano technology is used to describe a set of technologies that are based on physical, chemical and biological phenomena occurring at nano scale (1 – 100 nm).

BASIC CONCEPTS OF NANO-SCIENCE AND NANO-TECHNOLOGY

Nano-science is a convergence of physics, material science and biology which deals with manipulation of materials at atomic and molecular scales. While Nano-technology is the ability to observe measure, manipulate, assemble, control and manufacture matter at the Nano meter scale.

Or

Nano science and Nano technology involve the ability to see and to see and to control individual atoms and molecules.

SYNTHESIS OF NANO MATERIALS

There are two approaches for synthesis of Nano materials.

1. Top down approach
2. Bottom up approach

TOP DOWN APPROACH

Break down of bulk material into Nano material is called top down approach.

Or

Macro particles are converted into micro particles.

In this synthesis destructive method is used. The larger molecule (bulk material) decomposed into a smaller molecule and then these smaller molecules transform into the nanoparticles.

Ex: grinding, milling, PVD, lithographic method,

In this approach the starting material is in solid state.

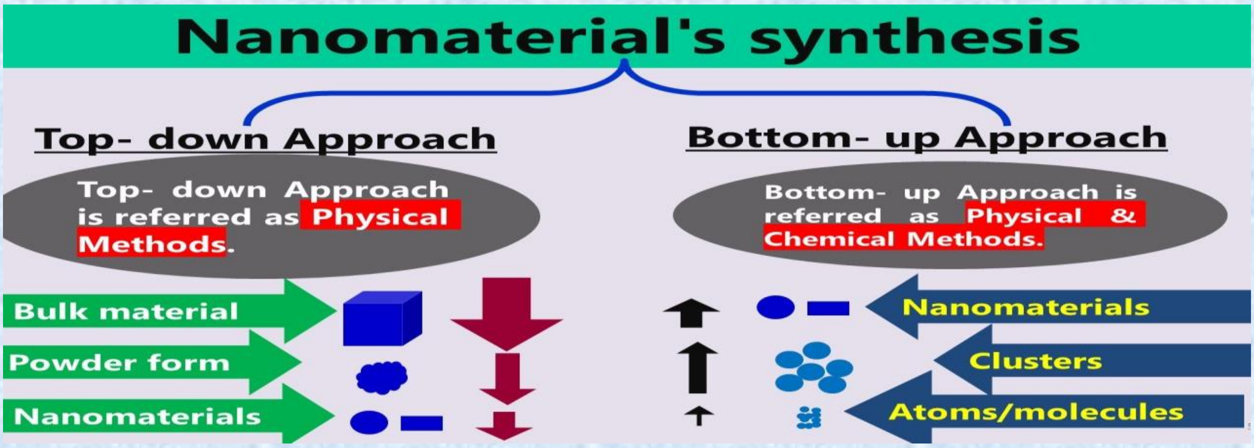
Ex: e-beam lithography, atomic force manipulation.

BOTTOM UP APPROACH

Atoms or molecules are converted to Nano particles which is called bottom up approach.

In this approach the starting material is either gaseous or liquid state of matter.

Ex: CVD, sol-gel, spinning, pyrolysis.



CLASSIFICATION OF NANO MATERIALS

Nano materials are categorized into four ways

1. Inorganic based Nano materials
2. Carbon based Nano materials
3. Organic based Nano materials
4. Composite based Nano materials

According to Siegel, Nano structured materials are classified as

1. Zero dimensional 0D
2. One dimensional 1D
3. Two dimensional 2D
4. Three dimensional 3D

0D → all X,Y,Z dimensions in nano scale

1D → one of the dimension (say X) is 100s of nm like nano wire, tubes etc.

2D → two of the dimensions say X,Y are in 100 s of nm scale like nano plates, belts

3D → where all x,Y,Z dimensions are large or more than 100 nm.

APPLICATIONS OF NANO MATERIALS

Nano materials are used increasingly in catalysis to boost chemical reaction. This reduces the quantity of catalytic materials necessary to produce desired results, saving money and reducing pollutants.

1. In medicine
   Targeted drug delivery, reduces side effects, early diagnosis of disease.
2. In electronics
   Reduce power consumption, less size and weight of components, smaller and faster processes.
3. In energy
   Reduce cost of catalysts in fuel cells, can increase efficiency of solar cells, increased energy density of batteries.
4. In space technology
   Light weight spacecraft, reduction of rocket fuel, larger the material strength.
5. In automobile
   High strength of metal, increased fuel efficiency, quality of paints
6. Environment
   Sensors detecting pollution level, harmful emission can be controlled.
7. In textiles
   Water repellent clothes, wrinkle free clothes.
8. In diagnosis
   DNA segment, genetic sequencing, specific drug delivery.

PROPERTIES OF NANO MATERIALS

1. Nano material exhibit different color depending upon their size.
2. Nano material when irradiated with UV light, emit visible light.
3. Melting point of Nano material is lower than melting point of bulk.
4. Reactivity of Nano material is more than that bulk material.

PHYSICAL PROPERTIES OF NANO MATERIALS

Physical properties of Nano materials are dependent on size, shapes (spheres, rods, platelets etc.) composition, crystal structure (FCC, BCC etc.) surface ligands or capping agents, the medium in which they are dispersed.

CHEMICAL PROPERTIES OF NANO MATERIALS

Chemical properties of Nano materials also change at Nano scale. As the percentage of surface of atoms in nanoparticles is large compared with bulk objects, therefore reactivity of Nano materials are more than bulk materials.

SYNTHESIS OF NANO MATERIALS

There are three methods

1. Physical method or top down approach or bulk to Nano particles
    a) Mechanical Ex: High energy ball milling, melt mixing
    b) Vapor Ex: physical vapor decomposition, electric arc
2. Chemical method or bottom up approach or small to bulk
   Ex: sol-gel, colloids
3. Biological method
   Ex: plant extract, DNA, enzymes, microorganisms.

CHEMICAL SYNTHESIS OF NANOPARTICLES

1. Precipitation method
2. Co-precipitation method
3. Sol-gel method

PRECIPITATION METHOD

Chemical precipitation method is a simple technique. This method is given more priority due its low cost an easy industrialization with improved reproducibility. This method offer low temperature growth and scale-up fabrication which yields colloidal solutions with wide range of particle distribution.

Metal oxides nanoparticles are prepared through this method. The method involves the precipitate of nanomaterial sized particles with in a continuous fluid solvent.

Ex 1

PREPARATION OF COPPER OXIDE NANOPARTICLES

55 grams of copper sulphatepentahydrate ($CuSO_4.5H_2O$) is mixed with 25 grams of hydroxyl ammonium chloride ($NH_2OH.HCl$) in 125 mL of distilled water. The mixture is cooled in a cold water bath with constant swirling. To this cold mixture a solution containing 40 grams of sodium hydroxide in 750 mL distilled water is added. The precipitate is settled down and the supernatant liquid is poured off. The precipitate is washed several times with distilled water until it is chloride free. The precipitate is dried at 200 – 250 ^{0}C (moisture content will evaporate). When the precipitate is heated to 300^{0}C in open air copper oxide is formed.

Ex 2

PREPARATION OF IRON (III) OXIDE NANOPARTICLES

Required chemicals

1. 0.2M $FeSO_4.2H_2O$
2. 0.1M $FeCl_3.6H_2O$
3. Deionized water
4. 3M Ammonia

PROCEDURE

In a beaker 0.4 grams of ferrous sulphate and 1.4 grams of ferric chloride are dissolved in 50 mL deionized water placed in magnetic stirrer. To this 3M ammonia is added dropwise with constant stirring at 1000 rpm till the PH reaches 10. In this time yellow precipitate changes to black precipitate. This black precipitate is filtered and dried in a hot air oven up to 2 hours. Fe_3O_4 nanoparticles are formed.

CO PRECIPITATION METHOD

This technique involves the precipitation of metal in the form of hydroxide from a salt precursor with the help of a base in a solvent.

It is an easy method for the synthesis of nanoparticles. Nanoparticle are obtained by this method usually have smooth surfaces, high yield. Nanoparticles are obtained without the aid of any surfactant material operated at low temperature. Reactions involve the simultaneous occurrence of nucleation, growth, coarsening and agglomeration process.

Ex: **Preparation of zinc rods**

In this method firstly two precursors are prepared. First precursor is zinc acetate dihydrate and second one is sodium hydroxide solution.

In this method zinc acetate dihydrate (4.18 grams of zinc acetate dehydrate is dissolved in 220 mL of methanol) solution is taken in a beaker. To this second precursor solution i.e. sodium hydroxide solution (1.45 grams of sodium hydroxide pellets are dissolved in 120 mL methanol) is added drop wise and it is stirred continuously, in this time milky colour solution is formed at the start of the reaction after 15 – 20 minutes milky color disappear. After 2 hours 2 minutes (synthesis time) stirring again white color zinc oxide precipitate is formed. This precipitate is filtered and dried in an oven zinc oxide nanoparticles are formed.

SOL-GEL METHOD

This process involves the transition of a solution from a liquid (sol) into a solid (gel) phase. Metal oxides are prepared through this method. The starting materials used in the preparation of the sol are usually inorganic metal salt or inorganic compound such as metal alkoxides.

Steps involved in sol-gel method

1. Hydrolysis (sol is formed)
   Metal alkoxide is converting into metal hydroxide
2. Condensation(in this process sol is converted into gel)
   When sol is kept undisturbed condensation takes place and it gets converted into gel.
3. Drying

Ex:

PREPARATION OF ZINC OXIDE NANOPARTICLES

Required materials

1. Zinc acetate dihydrate
2. Sodium hydroxide
3. Absolute ethanol

PROCEDURE

1. 20 grams of zinc acetate dihydrate is mix into 150 mL distilled water and stir for 20 minutes at 35^{0}C to produce zinc acetate solution.
2. 80 grams of sodium hydroxide pellets is mix into 80 mL distilled water and stir for around 20 minutes at 35^{0}C to form sodium hydroxide solution.

In this procedure the above two solutions are mixed in a beaker. To this mixture solution add 100 mL of ethanol into the drop-wise manner accompanied by vigorous stirring for 90 minutes for a gel like product. Dry this gel at 80^{0}C overnight and calcify in an oven at 250^{0}C for four hour and obtain zinc oxide nanoparticles.

PHYSICAL SYNTHESIS OF NANOPARTICLES

1. Inert gas condensation
2. **Aerosol method**

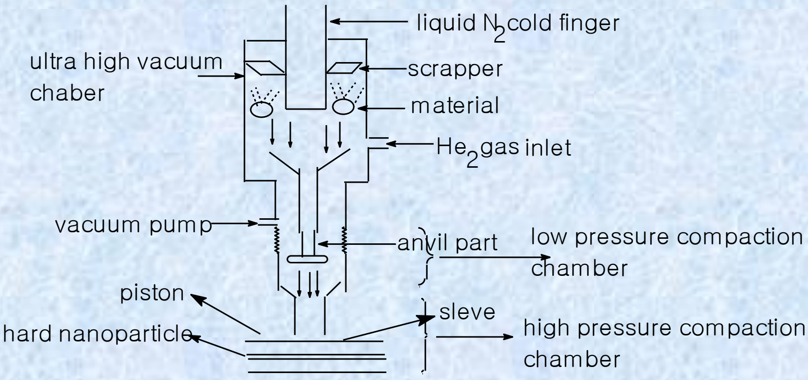
INERT GAS CONDENSATION METHOD

In this method material is heated at a temperature higher than its melting point. We can get vapours of material. Those vapors are again converted to bulk material by condensation method and finally we get our nanoparticles.

This method is used to get metallic or metal oxide nanoparticles.

Procedure

Material is heated above its melting point. Material is changes to vapor. These vapors will colloid with helium gas (inert gas) and they lose energy. Then they are absorbed on the surface of cold finger by using scraper, they are moved to the anvil through funnel. By using scraper they are moved to the anvil through funnel. Low pressure is applied to make bulk material. After that the bulk is sent to sleeve and high pressure is applied by using piston. We get hard nanoparticles of desired shape and size.



INERT GAS CONDENSATION METHOD

Aerosol method

In this method the precursors are transported to the substrate by means of a liquid / gas aerosol, which can be generated ultrasonically. This technique is suitable for use with non-volatile precursors.

In drug tablets, fumed silica serves as an excipient material. Aerosol is found in cosmetics from powered makeup to hair sprays as well as in light guides for telecommunications. Zinc oxide is a vulcanizing agent in the cutting of rubber.