# UNIT-5

## Material Science and Engineering

**Nano materials:**

Nano materials can be metals, ceramics, polymeric materials or composite materials. Nano particles are particles within the size ranging from 1-50nm and nano materials having the components less than 100nm at least in one dimension. Typical nanomaterials include

1.      Zero dimension nano structures, such as metallic, semi conducting and ceramic nano particles

2.      One – dimension nano structures, such as nano wires, nanotubes and nano rods.

3.      Two-dimension nano structures, such as  graphene, nanofilms, nanolayers, and nanocoatings

4.      Three – dimension nano materials such as  bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers.
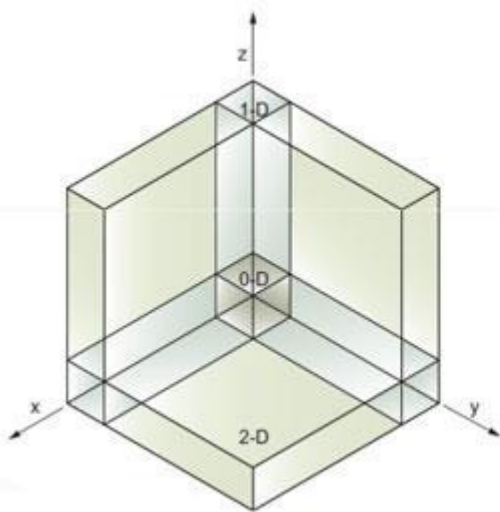


0-D:    All dimensions at the nanoscale

1-D:    Two dimensions at the nanoscale, one dimension at the macroscale

2-D:    One dimension at the nanoscale, two dimensions at the macroscale

3-D:    No dimensions at the nanoscale, all dimensions at the macroscale

**Preparation of Nano materials**:

Nano materials can be synthesized in a number of ways various methods employed for the synthesis is as follows:

i. **Sol-gel process:** It involves hydrolysis followed by condensation. A metal or metalloid is dispersed in acid or water to form a Sol (Finely divided solid particles dispersed in liquid). Gel is obtained from this sol by the removal of water (Gel is dispersion of a liquid throughout solid matrix).

$$MOR + H_2O \rightarrow MOH + ROH \text{ (hydrolysis)}$$

Metal alkoxide

**Various steps involved as follows:**

i. First the solvated solution of the alkoxide or metal is formed.

ii. Solvation is followed by poly condensation due to the formation of oxide or alcohol-bridged network. This leads to gelation.

iii. The gel solidifies and smaller particles aggregate to form larger particles.

This is followed by drying of the gel (water and volatile liquids are removed from the gel).

After this the surface bound to M-OH groups are removed so that gel is stabilized against rehydration

**TEM method (Transmission electron microscopy):**

Principle: TEM operates on the same basic principle as light microscope but uses electrons instead of light. When an electron beam passes through a thin-section specimen of a material, electrons are scattered. A sophisticated system of electromagnetic lenses focuses the scattered electrons into an image or a diffraction pattern, or a nano analytical spectrum

depending on the mode of operation.

Working: The beam of electrons from the electron gun is focused into a small, thin coherent beam by the use of the condenser lens. This beam is restricted by the condenser aperture, which exclude high angle electrons. The beam then strikes the specimen and part of it is transmitted depending upon the thickness and electron transparency of the specimen. This transmitted portion, is focused by the objective lens into an image on phosphor screen or charge coupled device (CCD) camera. The image then passed down the column through the intermediate and projector lenses, is enlarged all the way.
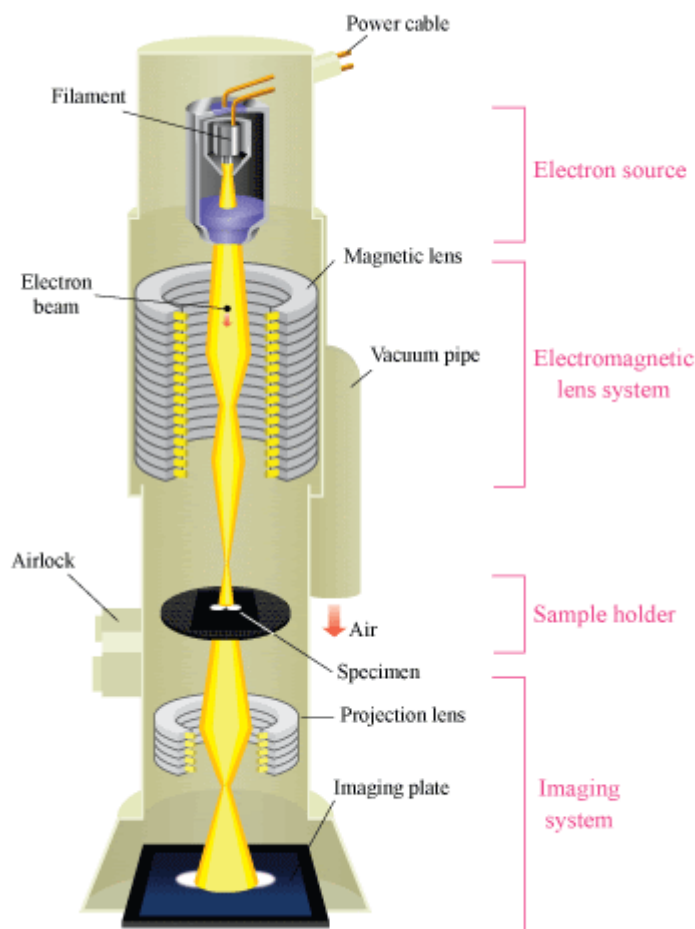
TEM Applications

1. A Transmission Electron Microscope is ideal for a number of different fields such as life sciences, nanotechnology, medical, biological and material research, forensic analysis, gemology and metallurgy as well as industry and education.

2. TEMs provide topographical, morphological, compositional and crystalline information.

3. The images allow researchers to view samples on a molecular level, making it possible to analyze structure and texture. This information is useful in the study of crystals and metals, but also has industrial applications.

4. TEMs can be used in semiconductor analysis and production and the manufacturing of computers.

**Carbon nanotubes:**

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Each carbon in a carbon nano tube is $SP^2$ hybridized and each atom is joined to three neighbouring atoms. CNT's can be single walled or multiwalled.
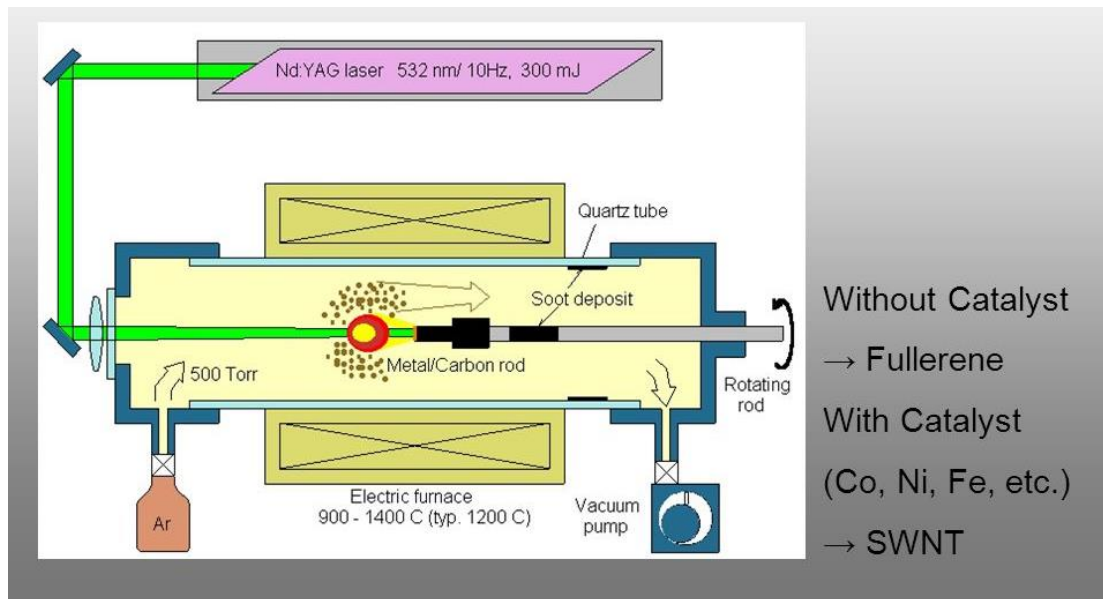
i) Single-walled carbon nano tubes (SWCNT's): These are long wrapped graphene sheets with length to diameter ratio of 1000. It can be obtained by wrapping one atomic layer of graphene.

ii) Multi-walled carbon nano tubes (MWCNT's): They consist of concentric SWCNT's with different diameters with an inter layer spacing of 3.4A0. MWCNT's have more than one surface with in it.

**Synthesis of Carbon nanotubes:** Carbon nanotubes are produced by three main techniques as follows:

1.  **Arc discharge:** This method is used for producing $C_{60}$ fullerenes. Nanotubes are created through arc vapourisation of two carbon rods placed end to end to end separated approximately by 1mm. In a enclosure fitted with inert gas (He, Ar) of 50 to 100 A, driven by approximately 20V creates a high temperature discharge. vapourises one of the carbon rod and forms a small rod shaped deposits on other rod.
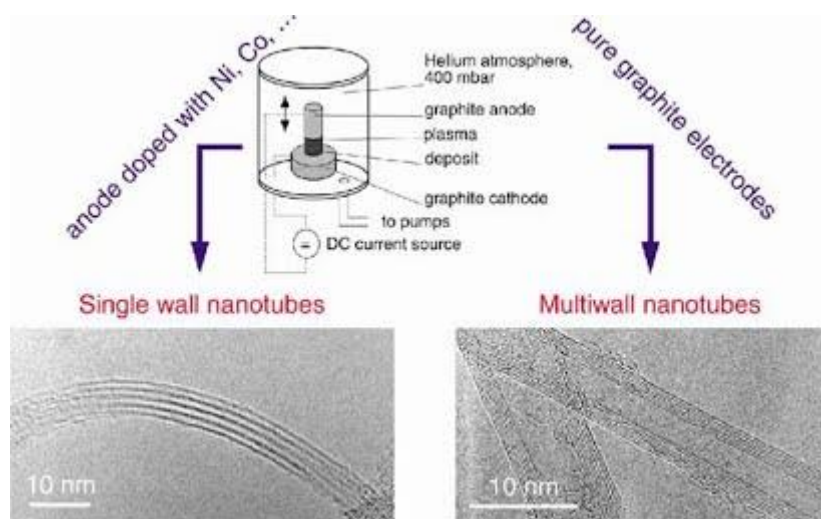


2.  **Laser ablation method:** A pulsed or continous laser is used to vapourise a graphite target in an oven $1200^0C$. Then oven is fitted with helium or argon gas in order to keep pressure at 500 Torr. A very hot plume forms, then expands and cools rapidly. As the vapourised species cool, small carbon molecules and atoms quickly, condense to form a large clustures.

Figure labels: Nd:YAG laser 532 nm/ 10Hz, 300 mJ; Quartz tube; Soot deposit; Metal/Carbon rod; 500 Torr; Rotating rod; Ar; Electric furnace 900 - 1400 C (typ. 1200 C); Vacuum pump; Without Catalyst → Fullerene; With Catalyst (Co, Ni, Fe, etc.) → SWNT

### 3. Chemical vapour deposition [CVD]:

CVD synthesis is achieved by putting a carbon source in the gas phase and using a energy source, such as plasma or a resistive heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include Methane, Carbon monoxide and Acetylene. The energy source is used to "crack" the molecule into reactive atomic carbon. Thus the carbon diffuses towards the substrate which is heated and cooled with a catalyst( usually a first row transition metal such as Ni, Fe or Co) where it will bind. Excellent alignment, as well as positional control on nanometer scale, can be achieved by using CVD. Control over the diameter as well as growth rate of the nanotubes can also be maintained.

**Chemical Vapor Deposition (CVD)**
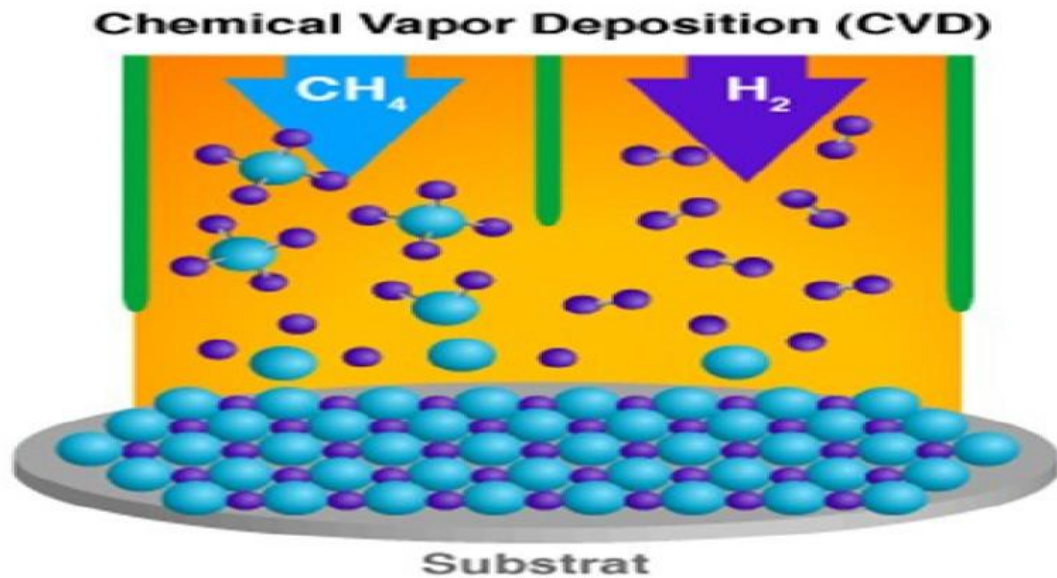
**Properties of carbon nanotubes (CNT):**

 **1. Strength:** Carbon nanotubes are the strongest, flexible and stiffest material in terms of tensile strength and elastic modulus respectively. This strength results from the covalent $SP^2$ bonds formed between the individual carbon atoms. CNT's are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to under buckling when placed under compressive, torsional or bending stress.

2. Hardness: The hardness (152 Gpa) and bulk modulus (462-546 GPa) of CNT'S are greater than diamond which is considered the hardest material. There are two things that account for their strength due to the interlocking carbon to carbon covalent bonds and CNT is one large molecule.

3. Electrical Properties: Because of symmetry and unique electronic structure of graphene the structure

a)     CNT's are one of the strongest and stiffest materials known, in terms of tensile strength and elastic modulus respectively.

b)     Young's modulus is in the range 1-5 TPa(Tera Pascal) for single walled CNT's and the tensile strength is about 150GPa for multi walled CNT's.

c)     CNT's can be either metallic or semi conducting depending upon the chirality.

d)     CNT's are known to exhibit super conductivity below 200C.

e)     CNT's will be able to achieve conductivities 20 times more than that of copper. The temperature stability of CNT's is estimated to be up to 28000C in vacuum and about 7500C in air.

e) CNT's will be able to achieve conductivities 20 times more than that of copper. The temperature stability of CNT's is estimated to be up to $2800^0C$ in vaccum and about $750^0C$ in air.

## Applications of CNT's:

1) In conducting polymers.

2) In electronics such as memory, semiconductor components and transparent conducting films for touch screens, displays and solar cells.

3) They can act as unique catalyst in various industrial chemical reactions.

4) CNT's are effective for controlled drug delivery and distribution of drugs inside the body.

5) Hydrogen can be strored in the carbon nontubes which in turn used for fuel cells. CNT's can replace platinum as catalyst in fuel cells.

6) CNT's are used for the treatment of cancer.

Properties of fullerenes

## Properties:

1. The $C_{60}$ molecule is extremely stable, being able to withstand high temperatures and pressures. The exposed surface of the structure is able react with other species while maintaining the spherical geometry.

2. The hollow structure is also able to entrap other smaller species such as helium, while at the same time not reacting with the fullerene molecule. In fact the interior of most buck balls is so spacious; they can encase any element from the periodic table

3. Bucky balls do not bond to one another. They do however; stick together via Van der Waals forces.

1. By doping fullerenes, they can be electrically insulating, conducting, semiconducting or even superconducting.

**SEM method (Scanning electron microscopy)**:

Basic principle: When the beam of electrons strikes the surface of the specimen and interacts with the atoms of the sample, signals in the form of secondary electrons , back scattered electrons and characteristic X-rays are generated that contain information about the samples surface topography and composition etc.

SEM images gives information about

i) Topography: Texture / Surface of a sample.

ii) Morphology: Size ,Shape, order of particles.

iii) Composition: Elemental composition of sample.

iv) Crystalline structure: Arrangement present within the sample.

Topics missing Green chemistry

What is green chemistry

By the mid-20th century, some of the long-term negative effects of these advancements could not be ignored. Pollution choked many of the world's waterways and acid rain deteriorated forest health. There were measurable holes in the earth's ozone. Some chemicals in common use were suspected of causing or directly linked to human cancer and other adverse human and environmental health outcomes.

Green chemistry takes the EPA's mandate a step further and creates a new reality for chemistry and engineering by asking chemists and engineers to design chemicals, chemical processes and commercial products in a way that, at the very least, avoids the creation of toxics and waste.

Sustainable and green chemistry in very simple terms is just a different way of thinking about how chemistry and chemical engineering can be done. to reduce waste, conserve energy, and discover replacements for hazardous substances. It's important to note that the scope of these of green chemistry and engineering principles go beyond concerns over hazards from chemical toxicity and include energy conservation, waste reduction, and life cycle considerations such as the use of more sustainable or renewable feedstocks and designing for end of life or the final disposition of the product.

Developed by Paul Anastas and John Warner*, the following list outlines an early conception of what would make a greener chemical, process, or product.

1. **Prevention:**

**It is better to prevent waste than to treat or clean up waste after it has been created.**

2. **Atom Economy**

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

### 3 Less Hazardous Chemical Syntheses

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

### 4. Designing Safer Chemicals

Chemical products should be designed to preserve efficacy of function while reducing toxicity.

### 5.Safer Solvents and Auxiliaries

The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.

### 6. Design for Energy Efficiency

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

### 7. Use of Renewable Feedstocks

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

### 8. Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or

avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis**

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation**

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

11. **Real-time analysis for Pollution Prevention**

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

12. **Inherently Safer Chemistry for Accident Prevention**

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

Green Solvents
*Green solvents* are environmentally friendly solvents, or biosolvents, which are derived from the processing of agricultural crops. The use of petrochemical solvents is the key to the majority of chemical processes but not without severe implications on the environment. Green solvents were developed as a more environmentally friendly alternative to petrochemical solvents. Ethyl lactate, for example, is a green solvent derived from

processing corn. Ethyl lactate is the ester of [lactic acid](#). [Lactate ester](#) solvents are commonly used solvents in the paints and [coatings industry](#) and have numerous attractive advantages including being 100% biodegradable, easy to recycle, noncorrosive, noncarcinogenic, and nonozone-depleting. Ethyl lactate is a particularly attractive solvent for the coatings industry as a result of its high solvency power, high boiling point, low [vapor pressure](#), and [low surface tension](#). It is a desirable coating for wood, [polystyrene](#), and metals and also acts as a very effective [paint stripper](#) and graffiti remover. Ethyl lactate has replaced solvents such as [toluene](#), [acetone](#), and [xylene](#), resulting in a much safer workplace.

Catalyst' is defined simply as a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change.

Catalysis is a key technology to achieve the objectives of sustainable (green) chemistry. Green catalysts are the catalysts which are eco friendly , can be regenerated hence reused multiple times and thus minimise waste production during process.
Large amounts of waste are generated every day by chemical processes. In particular, using stoichiometric equivalents creates unwanted byproducts like inorganic salts. Stoichiometric chemical procedures are increasingly being replaced by more efficient catalytic alternatives, empowering chemists to reduce energy and resource consumption. Greener catalysis means moving away from stoichiometric processes to homogenous and heterogeneous catalytic reactions using organic, organometallic, inorganic and biological catalysts.

## Ibuprofen

The synthesis of ibuprofen, a widely used anti-inflammatory compound, was reduced from six stoichiometric steps to three catalytic steps. The six-step stoichiometric reaction was inefficient; more than half of the ingredients became waste or byproducts rather than the desired compound. This new synthesis increased the efficiency of the reaction and reduced waste.

Similarly, benzene and propene are converted into cumene in the [manufacture of phenol](#).  This reaction needs an acid catalyst, such as

aluminium chloride.  A solid zeolite with acid groups, such as ZMS-5 is now the favoured catalyst:
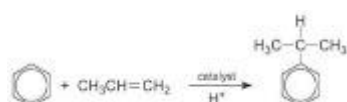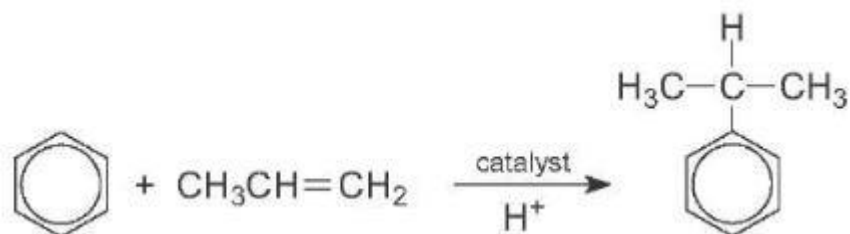




The zeolite is more evironmentally friendly as the effluent is much cleaner and lower temperatures and pressures can be used.


## *Less hazardous chemical synthesis*
The family of polycarbonates contains very important polymers which are used where high optical properties combined with strength are needed. The polycarbonate most used is manufactured from bisphenol A, whose structure is:
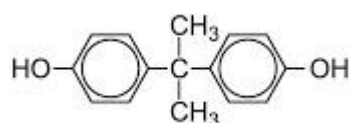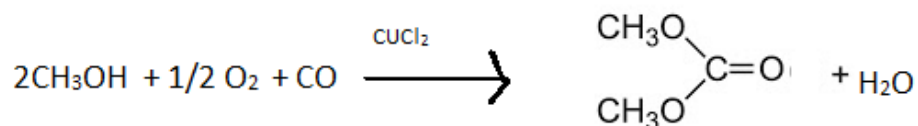


The polycarbonate is manufactured by a condensation reaction between bisphenol A and either carbonyl chloride or diphenyl carbonate.

Carbonyl chloride is a very poisonous gas, manufactured from other hazardous gases, carbon monoxide and chlorine:

$$CO(g) + Cl_2(g) \longrightarrow \underset{Cl}{\overset{Cl}{\diagdown}} C=O \ (g)$$

$$(COCl_2)$$
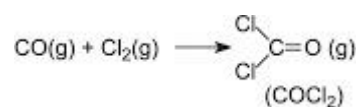
On the other hand, diphenyl carbonate is produced from dimethyl carbonate, which is readily manufactured from methanol, carbon monoxide and oxygen in the liquid phase, in presence of copper(II) chloride, $CuCl_2$:

$$2CH_3OH(l) + \tfrac{1}{2}O_2(g) + CO(g) \xrightarrow{CuCl_2} \underset{CH_3O}{\overset{CH_3O}{\diagdown}} C=O(l) + H_2O(l)$$

dimethyl carbonate

$$2CH_3OH + 1/2\ O_2 + CO \xrightarrow{\ \ CUCl_2\ \ } \underset{CH_3O}{\overset{CH_3O}{\diagdown}} C=O \ + H_2O$$

Dimethyl carbonate, when heated with phenol in the liquid phase, forms the diphenyl carbonate:
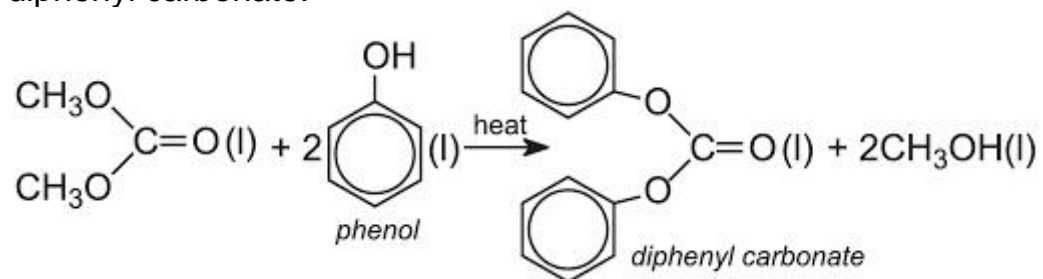


Overall, the process for the production of polycarbonate that uses diphenyl carbonate is less hazardous than that using carbonyl chloride.