NANO MATERIALS

Nanomaterials are materizes possessing grain sizes on the order of a billionth of a meter ~~(10)~~ 10^{-9} (10^{-9} of a meter).

→ Nanomaterial (nanocrystalline material) has grains on the order of 1-100 nm. The average size of an atom is on the order of 1 to 2 angstroms (Å) in radius.

→ 1 nanometer comprizes ~~of~~ 10 Å, and hence in one nm, there may be 3-5 atms, depending on the ~~ion~~ atomic radii.

→ Particles of metals, semiconductors or ceramics having diameters in the range 1-50 nm constitute nanoclusters. The clusters are characterized by a large surface area to volume ratio which implies that a large fractions of atoms resides at the grain boundary. Physical properties of such clusters correspond neither to those of the free atoms or molecules making up the particles, nor to those of bulk solids of the same composition.

→ Nanomaterials are exceptionally strong, hard, ductile at high temperature, corrosion resistant and chemically very active.

→ Nanomaterials are prepared by physical (Evaporation in ~~inert gas~~ inert gas atmosphere, laser pyrolysis sputtering techniques) and chemical methods (Spray technique, precipitation, sol-gel method etc.)

→ Nanophase materials are prepared by compacting the nanosized clusters generally under high vacuum. The average grain sizes in these materials range from 5-25 nm.

- Nanoparticles of oxide materials can be prepared by the oxidation of fine metal particles, by spray techniques, by precipitation or by sol-gel method.
- Cluster of carbon metals and metal ~~oxides~~ carbides (for e.g. M_8C_{12}, M = V, Zr, Hf or Ti) etc. are prepared by laser ablation.
- Nanocomposites as distinct from nanophase (multiphase) solid materials with ~~one~~ at least one dimension in the nanometer range. These composites lead to nanophasic or multiphasic ceramics, glasses or porous materials with tailored and improved properties. They can be derived from sol-gel, intercalation or entrapment.

(Dr. Kalpana Maheria, ACD)

APPLICATIONS OF NANOMATERIALS

1. Next generation computer chips
2. Kinetic Energy (KE) penetrators with enhanced lethality
3. Better insulation materials
4. Phosphors for high definition TV
5. Low cost flat panel displays
6. Tougher and harder cutting tools
7. Elimination of pollutants
8. High energy density batteries
9. High power magnets
10. High sensitivity sensors.
11. Automobiles with greater fuel efficiency
12. Aerospace components with enhanced performance characteristics
13. Better and future weapons platforms
14. Longer lasting satellites
15. Longer lasting medical implants
16. Ductile machinable ceramics
17. Large electrochromic display devices

Basics of Green Chemistry

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Green chemistry introduced in early 1990's, is a way of using basic science to address environmental issues in an economically profitable manner and goes by many names, "Environmentally Benign chemistry", "Clean chemistry", "Atom Economy", Benign by design chemistry and sustainable chemistry.

→ Green chemistry accomplishes both economic and environmental goals simultaneously through the use of sound, fundamental scientific principles.

The term green chemistry is adopted by the IUPAC working party on synthetic pathways and processes in green chemistry is defined as;
"The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substance".
Green chemistry by the design of environmentally compatible chemical reactions, offers the tools to approach pollution and sustainability concern at the source.

Environmentally benign synthesis or "green chemistry seeks to incorporate environmental and toxicological awareness at the design phase of synthetic process. The basic concept is that it is far better to develop a synthetic strategy that avoids the use of hazardous materials in the first place than to face clean up containment and waste disposal.

→ Interest in green chemistry was first initiated in US after the passage of the Pollution Prevention Act of 1990. Subsequently, the environment protection agency (EPA) got involved in green chemistry.

* Twelve Principles of Green Chemistry:

The principles of Green Chemistry are a significa[nt] beginning for the chemical profession in dealing with this novel concept for the betterment of the environment. The twelve principles of Green Chemistry proposed by Paul ~~Anad~~ Anastas and John Warner include all aspects on the product and the production level from prevention to the design of more efficient synthesis, from the design of les hazardous substances to the use of renewable feed stocks.

1. The basic principles of "GREEN CHEMISTRY" are as follows;

1) Prevention: It is better to prevent waste than to treat or ~~ct~~ to clean up waste, after it is formed.

2) Atom Economy: Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3) Less hazardous chemical synthesis:
Whenever 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 effect their desire function while minimizing their toxicity.

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

6) Design of Energy Efficiency: Energy requirement of chemical process should be recognized for their environmental and economic impacts and ~~shoo sa~~ should be minimized. If possible, synthetic methods should be conducted a ambient temp. & Pressure.

7) Use of renewable feedstocks:
A raw material or feed stock should be renewable rather than depleting whenever technically and economically practicable.

8) Reduced Derivatives: Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical process) 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 harmless 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 ~~pro~~ prior to the formation of hazardous substance.

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.

A few Examples of Green Chemistry and Clean Technology:

i) Replacement of ozone depleting CFCs:-
Ozone depletion and the formation of ozone hole have been attributed to the release of chlorofluoro carbons used as refrigerants and blowing agents. The use of hydrocarbons and CFCs as blowing agents in the manufacturing of polystyrene foams has ~~bee~~ been completely replaced by green technology involving carbon dioxide as blowing agent.

Catalytic Converters: Automobile exhaust gases pass through catalytic converters in gasoline powered cars to reduces the VOCs, anthropogenic hydrocarbons and NO_x thereby preventing air pollution and photochemical smog.

Energy Saving: catalytic cracking in petroleum refineries is more energy efficient requiring a lower temperature and lower pressure as compared to thermal cracking.

Supercritical Carbon Dioxide as solvent:

The use of supercritical carbon ~~Dioxide~~ Dioxide in decaffenation of coffee and tea is well known. computer chip manufacture requires large amount of hazardous solvents such as HCl/H_2SO_4, halogenated hydrocarbons for removing photoresists. In addition final washing of the chips requires a large amount of purified water. A new alternative process called the supercritical carbon dioxide resist remover ~~CSO~~ (SCORR) has been developed using supercritical carbon dioxide as solvent for removing the photoresist. eliminating the use of hazardous solvents. Additional advantages of this method include the elimination of the washing step with high purity water and the recovery of carbon dioxide for recycling.

~~$ScCO_2$~~ Liquid CO_2 has a potential use as solvent with low environmental impact. It can dissolve many small organic ~~mo~~ molecules. However, large molecules (oils, polymers, waxes, greases & proteins) are insoluble in carbon dioxide. Suitable surfactants have been developed for dissolving these large molecules in CO_2 which has enabled the use of ~~Sa~~ $ScCO_2$ in dry cleaning ~~representing~~ replacing the presently used perchloroethylene ($Cl_2C=CCl_2$). Perchloroethylene is a VOC causing air pollution and also a ground water pollutant. It is also suspected to be a carcinogen. $ScCO_2$ can be recovered after the washing cycle by evaporation simply by ~~washing~~ reducing the pressure. The recovered gas can be liquefied and used once again for dry cleaning.

Elimination of hazardous reagents for synthesis.

Alkylation is an important reaction requiring the use of ~~to~~ hazardous aluminium chloride as catalyst. The catalyst can not be recovered and reused. zeolite catalysts and supported super acid catalysts have largely replaced aluminium chloride and are recovered in more ecofriendly process. Polycarbonate production involving the use of the hazardous reagent (phosgene) and solvent (methylene chloride) has been replaced by a solid state polymerization ~~process~~ process.

Another example is the manufacture of the pesticide carbaryl involved the use of phosgene and methyl isocyanate (Bhopal tragedy in 1984 is attributed to the release of this gas) The new synthetic route does not involve the use of either of these chemicals.

Use of renewable feedstock:

Biodiesel is obtained from oil obtained from renewable feed stock jatropa and similar plants. Biodiesel is free from nitrogen and sulphur containing compounds and when used as automobile fuel the exhausts are ~~free~~ free from oxides of Nitrogen and sulphur.

Glucose syrup obtained by the hydrolysis of corn starch is converted to lactic acid and polymerized. The polylactic acid is used for ~~the~~ the production of eco-plastics used for plastic containers, films and packaging materials.

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The concept of atom economy was developed by B. M. Trost. According to him, the % atom utilization is determined as follows -

$$\% \text{ Atom utilization} = \frac{\text{M.W. of desired product}}{\text{M.W. of (formed product + Waste product)}} \times 100$$

- The concept of atom economy was quantified by Roger A. Sheldon. According to Sheldon, the % atom economy was calculated as given below.

$$\% \text{ Atom economy} = \frac{\text{F.W. of atom utilised}}{\text{F.W. of all reactants used in its reaction}} \times 100$$

- Environment Factor (E-factor)

$$= \frac{\text{Amount of waste generated}}{\text{Amount of desired product generated}}$$

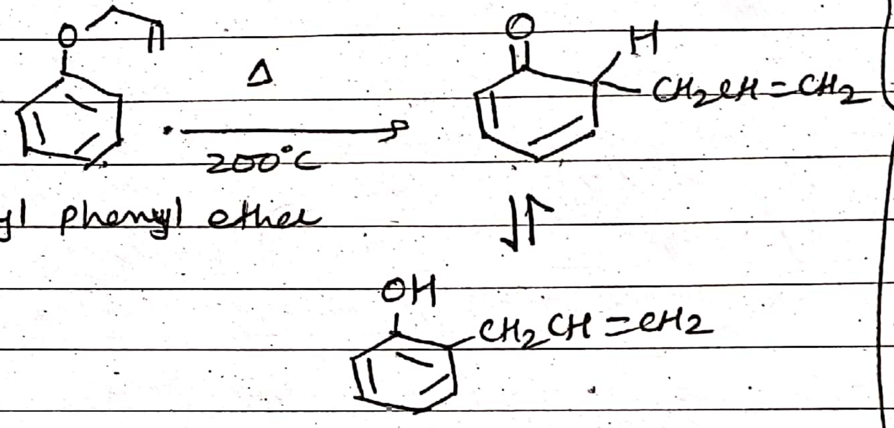
If value of E-factor is ≥ 1, reaction is useless.

- Higher the E-factor value, more is the waste and more -ve impact on environment

Reactions involved in organic synthesis are,

1) Rearrangement Reactions
2) Addition Reactions
3) Substitution Reactions
4) Elimination Reactions.

1 Rearrangement Reactions:



Allyl phenyl ether

O-Allyl phenol

Claisen Rearrangement

The reaction is 100% atom economical.

Reagent Formula	FW (g/mole)	Utilized Formula	FW	Unutilized Formula	FW.
$C_9H_{10}O$	134.173	$C_9H_{10}O$	134.173		

$$\% \text{ Atom economy} = \frac{134.173}{134.173} \times 100 = 100\%$$

100% atom economical reaction, since all the reactant is incorporated into final product (O-allyl phenol).

(2) Addition Reactions:

These reactions are also 100% atom economical.

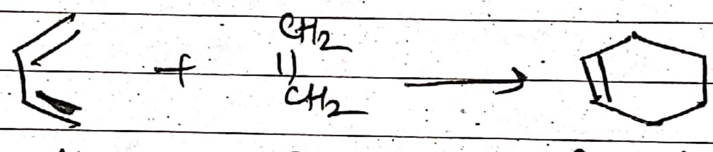
→ In these reactions, groups are added to a molecule usually across a double or triple bond.

For e.g (i) Catalytic Hydrogenation of Propene

$$CH_3-CH=CH_2 + H_2 \xrightarrow{Ni} CH_3CH_2CH_3$$

Propene — Propane.

(ii) Cycloaddition of butadiene and ethylene



Butadiene — Ethene — Cyclohexene.

(3) Substitution Reactions:

In substitution reaction, one atom (or group of atoms) is replaced by another atom (or group of atoms). The atom that is replaced is not utilized in the final product.

For eg.

$$CH_3-CH_2-\overset{O}{\overset{||}{C}}-OCH_2CH_3 + H_3C-NH_2 \longrightarrow$$

Ethyl propionate — Methyl amine

$$H_3C-CH_2-\overset{O}{\overset{||}{C}}-NH-CH_3 + HO-CH_2-CH_3$$

N-methyl propamide — Ethyl alcohol

Dr. KCM

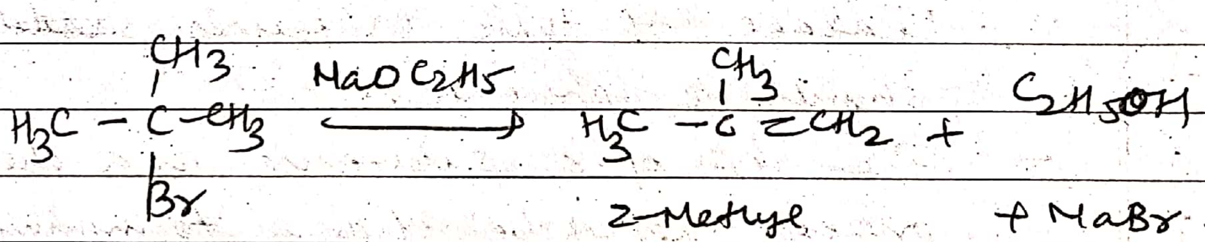
Reagent Formula	FW	Utilized Formula	FW	Unutilized Formula	FW
$C_5H_{10}O_2$	102.32	C_3H_5O	57.057	C_2H_5O	46.061
CH_5N	31.057	CH_4N	30.049	H	1.008
$C_6H_{15}NO_2$	133.189	C_4H_9NO	87.120	C_2H_6O	46.069

$$\% \text{ Atom Economy} = \frac{87.120}{133.189} = 65.41\%$$

(4) Elimination reactions.

In a elimination reaction, two atoms or ~~group~~ group of atoms are lost from the reactant to form a π bond.

For e.g. Dehydrohalogenation



2-Bromo-2-methyle propane

2-Methyle propane

% atom economy = 27 %

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9. Use of catalyst :-

It ~~is~~ should be preferred as it enhances the rate of reactions without its consumption.

Advantages are;

(i) Less consumption of energy
(ii) Time saving
(iii) % Atom economy may increase.
(iv). Minimum waste product formation

11. Prevention of accidents :

- The manufacturing plants should be so designed to eliminate the possibility of accidents during operations.
- The process should be safe and less hazardous.
- Leakage of toxic materials ~~should~~ should be prevented.
- The use of a substance in a chemical process should be chosen to minimize the potential for chemical accidents including explosions and fire.

12. Real time analysis for pollution.
(Strengthening of Analytical Techniques).

The procedure should be ~~be~~ monitored continuously and the formation of pollutants should be prevented in their initial stage during the reaction. This is in process monitoring and can control the pollution before its formation.