PREPARATION OF NANOMATERIALS

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- Molecular Sieves
- Nanosponges
- Ion Beam Induced Nanostructure

MOLECULAR SIEVES

- Molecular sieves are porous solids with pores of the size of molecular dimensions 0.3-2.0 nm in diameter.
- Some are crystalline with a uniform pore size delineated by their crystal structure.
- Molecular sieves often consist of alumino silicate minerals, clays, porous glasses, zeolites, synthetic compounds that have open structures through or into which small molecules such as nitrogen and water can diffuse.

Why They Are Used…

Use of Molecular sieves to dry, purify and separate liquids and gases prevents unwanted side reactions, helps meet product specifications and avoids costly complications from equipment corrosion and freeze up.

- ✓ Purification and Dehydration in one operation.
- ✓ Dehydration without adsorbing valuable product or altering the composition.
- ✓ High Product Recovery.
- ✓ Numerous purification and dehydration cycles are possible due to the reversible adsorption process.

- ✓ Dehydration to water content less than 0.1ppm.
- ✓ High capacity for water above 200°F (93°C)
- ✓ High cyclic capacity with sufficient thermal or pressure swing purging


DO NOT EAT
Contains Harmles
Silica Gel for
Moisture Absorben
DO NOT EAT
Contains Harmless


CONTAINER DESICCANT BAG
Protects cargo from moisture damage
Contains calcium chloride and clay minerals
Can be disposed of as normal waste
DO NOT EAT


PILLOWPAK


DESICCANT
MOLECULAR
DO NOT EAT

Evolution of Molecular sieve materials

Time of Initial Discovery

- Late 1940s to early 1950s
- Mid 1950s to late 1960s
- Early 1970s
- Late 1970s
- Early to mid 1980s
- Early to mid 1990s
- Late 1990s
- 2000s

Composition

- Low Si/Al ratio zeolites
- High Si/Al ratio zeolites
- SiO2 molecular sieves
- AlPo4 molecular sieves, Metallo silicates, aluminosilicates.
- AlPo4 based molecular sieves
- Metallophosphates, Mesoporous molecular sieves = octahedral and tetrahedral frameworks
- Metal organic frameworks
- UZM Aluminosilicates, Germanosilicates , SiO2 molecular sieves in fluoride media.

Applications

- Adsorbent for static dehydration in a closed gas or liquid system
- Used in the packaging of drugs, electronic components and perishable chemicals.
- Water scavenger in paint and plastic systems.
- Used commercially for general gas drying, air plant feed purification(simultaneous removal of H2O and CO2), and liquid hydrocarbon.
- Air dryers with a desiccant-type in-line filtration system supplies clean, dry air to truck air brake systems aiding in the prevention of air line freeze ups.

- Zeolite molecular sieves keep dual pane windows free of moisture and vapours.
- Zeolite molecular sieves are used to purify industrial gases and for the bulk separation of oxygen from air.
- Zeolite ions were used extensively in nuclear waste clean up after the Three Mile Island and Chernobyl nuclear accidents.
- Significant research reports on the use of zeolite as low dielectric materials for microprocessors.

Molecular Sieves used in Industries

Application

- Oxygen concentrators for respiratory patients.
- Air brakes
- Insulated glass (dual-pane windows)
- Deodorization

Role of Molecular sieves

- Adsorption of nitrogen from compressed air using a pressure or vacuum swing system to obtain oxygen purity up to 95%.
- Dehydration of compressed air on brake systems of heavy and medium-duty trucks, buses and trains.
- Removal of initial trapped moisture inside the dual-pane window and the moisture that will permeate during the life of the unit to prevent fogging
- Removal of odor or taste from personal-care products and plastics with high silica (hydrophobic) zeolite molecular sieves.

- Natural gas
  - Removal of sulfur compounds from ethane, propane and butane
  - Removal of water and sulfur compounds to protect gas transmission pipelines.
- Petroleum refining
  - Removal of water, HCl and H2S from reformer streams.
  - Separation of normal paraffins from branched chain and cyclic compounds.
- Petrochemicals
  - Removal of water, carbon dioxide, methyl alchohol and other oxygenates, hydrogen sulfide and sulfur compounds, ammonia and mercury from ethylene, propylene, butylenes, amylenes and various solvents and co-monomers

NANOSPONGES

- Nanosponge is about the size of a virus with a backbone (a scaffold structure) of naturally degradable polymer.
- The average diameter of a nanosponge is below 1µm but fraction below 500µm.
- Nanosponge could be in crystalline or paracrystalline form.
- Loading capacity of nanosponges depends mainly on degree of crystallisation. Paracrystalline nanosponges can show different loading capacity.

Chemicals used for preparation of Nanosponge

Polymers

- Hyper cross linked Polystyrenes, Cyclodextrins and its derivatives like Methyl β-Cyclodextrin, Alkyloxycarbonyl Cyclodextrins, 2-Hydroxy Propyl β-Cyclodextrins andCopolymers like Poly (valerolactone –allylvalerolactone) & Poly (valerolactone-oxepanedione) and Ethyl Cellulose & Poly vinyl acetate.

Cross–linkers

- Diphenyl Carbonate, Di-aryl carbonates, Di-isocyanates, Pyromellitic anhydride,Carbonyldi-imidazoles, Epi-chloridrine, Glutraldehyde, Carboxylic acid di-anhydrides, 2, 2- bis (acrylamido), Acetic acid and Dichloromethane

METHOD OF PREPARATION

- SOLVENT METHOD
- ULTRASOUND – ASSISTED SYNTHESIS

SOLVENT METHOD

1. The polymer can be mixed with a suitable solvent like polar aprotic solvent such as dimethyl formamide(DMF), dimethyl sulfoxide (DMSO).
2. The mixture is added to excess quantity of the cross-linker,preferably in cross-linker/polymer molar ratio of 1:4.
3. Then the reaction is carried out at temperature ranging from 10°C to the reflux temperature of the solvent, for time ranging from 1 to 48hour.
4. The solution is cooled at room temperature and the product is added to large excess of double-distilled water.
5. The recovery of the product is done by filtration under vaccum and subsequent purification by prolonged extraction with ethanol.
6. Drying the product under vacuum completes the process.

ULTRASOUND-ASSISTED SYNTHESIS

1. Nanosponges are obtained by reacting polymers with cross-linkers in the absence of solvent and under sonication.
2. The Nanosponges obtained by this method will be spherical and uniform in size.
3. The polymer is mixed with the cross-linker in a particular molar ratio in a flask,then placed in an ultrasound bath, filled with water and heated to 90°C.
4. Perform sonication for few hours then the mixture is cooled and break it small size and wash it for removing non reacted polymer.
5. Subsequently purify it by prolonged soxhlet extraction with ethanol for further drying.

LOADING OF DRUG INTO NANOSPONGES

1. Nanosponges were pretreated to obtain a mean size below 500nm.
2. Nanosponges is suspended in water and then sonicated to avoid the presence of aggregates.
3. Then the suspension is centrifuged to obtain the colloidal fraction.
4. The supernatent is separated and the sample is to be dried by freeze drying.
5. Aqueous suspension of nanosponge is prepared and dispersed in the excess amount of the drug and the suspension is maintained under constant stirring for specific time.
6. The drug from complexed drug is separated by centrifugation. Then, the solid crystals of nanosponges are obtained by solvent evaporation or by freeze drying.
7. The drug loading occurs as a mechanical mixture rather than inclusion complex

CHARACTERISATION OF NANOSPONGES

- Solubility studies
- Loading efficiency or Entrapment efficiency
- Microscopy studies
- Polydispersity Index & Particle size
- Zeta potential determination
- Infra-red Spectroscopy
- X-ray diffractometry
- Single crystal X-ray structure analysis

APPLICATIONS

- Cancer Therapy
- Oxygen delivery system
- As a carrier for biocatalysts and in the delivery and release of enzymes, proteins, vaccines and antibodies.
- In the removal of organic matter to produce ultrapure water for power regeneration
- Solubility enhancement
- Topical drug delivery system
- Antiviral application
- More effectiveness than direct injection
- Floriculture

ADVANTAGES

- Targeted site specific drug delivery
- Can be used to mask unpleasant flavours and to convert liquid substances to solids.
- Less harmful side effects (since smaller quantities of the drug have contact with healthy tissue).
- Nanosponge particles are soluble in water, so the hydrophobic drugs can be encapsulated within the nanosponge, after mixing with a chemical called an adjuvant reagent.
- Particles can be made smaller or larger by varying the proportion of cross-linker to polymer
- Easy scale-up for commercial production

- Production through fairly simple chemistry called "click chemistry" (methods for making the nanosponge particles and for attaching the linkers).
- The drug profiles can be tailored from fast, medium to slow release, preventing over- or under-dosing of the therapy.
- Predictable release
- Biodegradable.

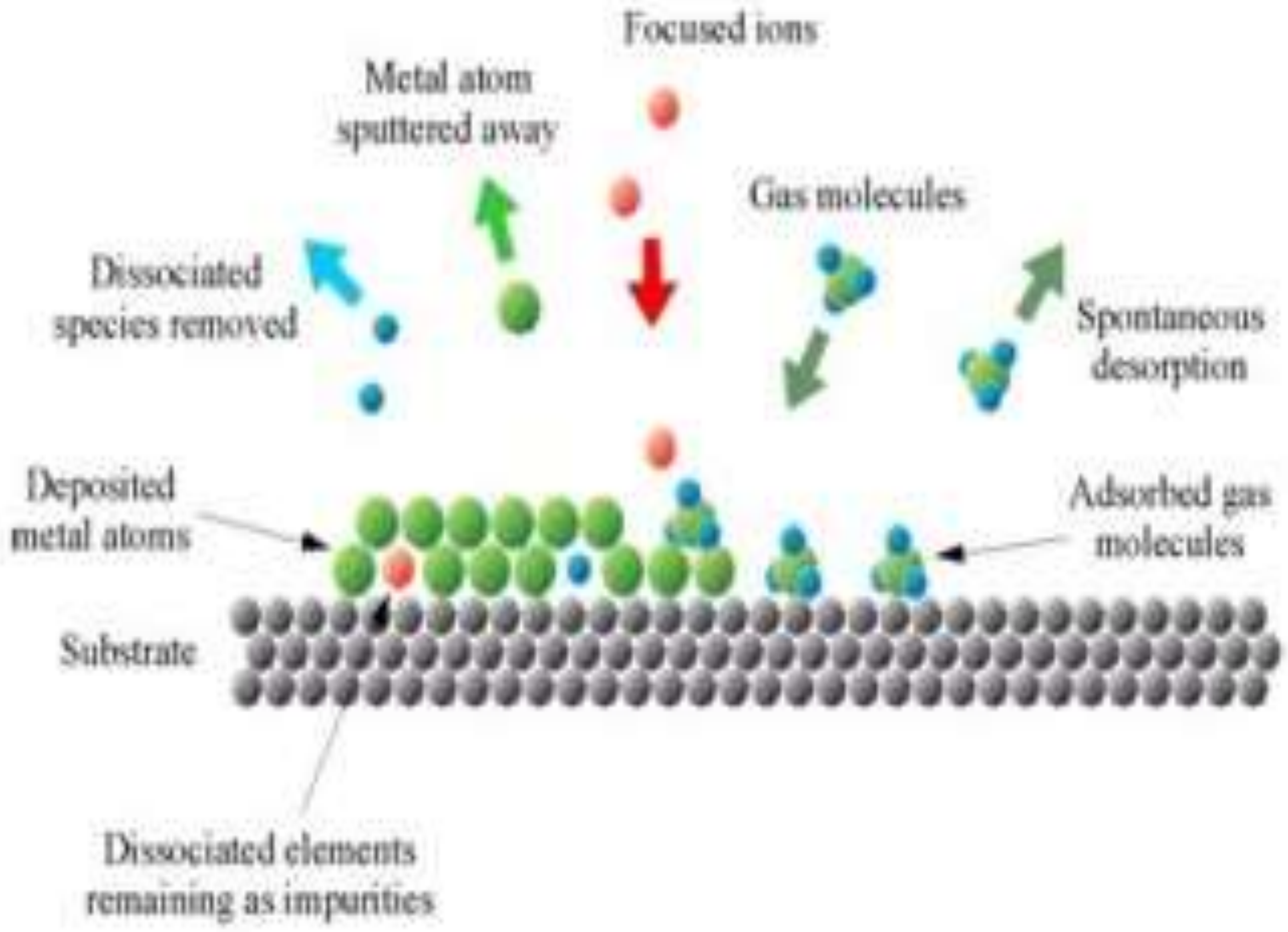
ION BEAM INDUCED NANO STRUCTURE

- Ion beams ranging from a few eV to MeV have been used to modify the thin film structures, synthesizing new structures, coating thin films, mixing immiscible layers, and for characterizing materials.

- When an energetic ion impinges on a solid material, many interesting phenomena can occur. Eg: sputtering of target material, surface and interface morphological changes, etc

- Ion beams requires a systematic study on ion irradiation with a control on separating nuclear and electronic energy loss regimes and under various irradiation parameters like fluence, dose-rate, substrate temperature, and geometry.

- Ion beams are used to fabricate various two-dimensional nanostructure devices such as single-electron transistors and metal–oxide–semiconductor (MOS) transistors with nanometer gate lengths.



1. Adsorption of the precursor molecules on the substrate
2. Ion beam induced dissociation of the gas molecules
3. Deposition of the material atoms and removal of the organic ligands

- Difference :The deposition rate of FIB is much higher than that of EB due to factors such as the difference in mass between an electron and an ion.
- the smaller penetration depth of ions compared with electrons makes it easier to create complicated three-dimensional nanostructures.
- Background : The high-energy ion beam is used to decompose the organometallic molecules adsorbed onto the surface of the substrate,it leads to the release of metal atoms,which incorporated onto the surface.
- The method involves a localized chemical vapor deposition process that is induced by an ion-beam.
- On the scanning action, nanowalls, nanorods, and multilayer nanostructures in various geometries and patterns can be formed.
- The use of an ion-beam also allows for the controlled directional growth of high-aspect ratio features.


Thank you