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A review on nanoporous materials and its industrial applications

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ABSTRACT

Nanoporous materials consist of a regular organic or inorganic framework supporting a regular, porous structure. The size of the pores is generally 100 nm or smaller. Most nanoporous materials can be classified as bulk materials or membranes. Activated carbon and zeolites are two examples of bulk nanoporous materials, while cell membranes can be thought of as nanoporous membranes. A porous medium or a porous material is a material containing pores (voids). The skeletal portion of the material is often called the “matrix” or “frame.” The pores are typically filled with a fluid (liquid or gas). There are many natural nanoporous materials, but artificial materials can also be manufactured. One method of doing so is to combine polymers with different melting points, so that upon heating, one polymer degrades. A nanoporous material with consistently sized pores has the property of letting only certain substances pass through while blocking others. The applications that nanoporous materials can be used for catalysis, separation and sensing, drug delivery, etc. They are used for encapsulating drugs and allowing for a slow controlled release of the drug and many more applications that have the ability to revolutionize the way medication, sensors and catalysis due to their unique properties.

Keywords: Nanoporous materials, Pores, Matrix, Zeolite, Aerogel, Catalysis, Drug delivery.

INTRODUCTION

Porous metals

A solid material that contains cavities, channels or interstices can be regarded as porous. Porous materials are of great interest in various applications, ranging from catalysis, adsorption, sensing, energy storage and electronics owing to their high surface area, tunable pore size, adjustable framework and surface properties. They are lightweight materials and have useful characteristics such as low bulk density, high surface area, low thermal conductivity, good penetrability, energy management use, noise attenuation, vibration suppression etc. [1-5]

The presence of pores in a material allows the material to have new properties that the bulk material does not have. Porous materials have porosity between 0.2to 0.95(volume ratio of pore space to total volume of material). [6-10]

Porosity influences the chemical reactivity of solid and the physical interaction of solids with

gases and liquids. High surface area porous materials are of great importance especially as catalyst, catalyst supports, thermal insulators, sensors, filters, electrodes and burner materials.
The science and technology of porous materials has progressed steadily and is expanding in many new directions with respect to processing methods and applications.

Porous ceramic materials are synthesized by various methods such as polymer sponge method, foam method, leaching, sintering of particles having a range of sizes, emulsion templating, gel casting, injection moulding, solgels process and heat treatment of a ceramic precursor containing carbon rich compound. Pores can have various shapes and morphology such as cylindrical, spherical and slit types.

Classification of pores

Based on the accessibility of an external fluid, pores can be classified in to closed pores and open pores. Closed pores are totally isolated from their neighbours and surface of the particle. They influence macroscopic properties such as bulk density, mechanical strength and thermal conductivity, but are inactive in processes such as fluid flow and adsorption of gases. Pores which have a continuous channel of communications with external surface of the body are called open pores [11-15].

In Fig. 1.1 region ‘a’ represents the closed pores, and regions such as b, c, d, e and f represent open pores.

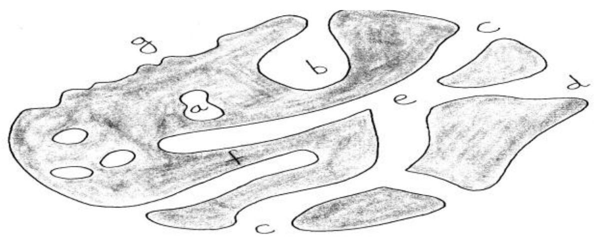


Fig: 1.1 Classification of pores

In the figure ‘b’ and ‘f’ (one end) are described as blind or saccate pores. Based on the pore size, IUPAC classified porous materials in to Microporous, Mesoporous and Macrporous as given below:

- Microporous materials (<2nm)
- Mesoporous materials (2-50nm)
- Macroporous materials (<50nm)

MICROPOROUS MATERIALS (<2NM)

Examples of microporous materials include zeolites and metal-organic frameworks (metal ions or clusters coordinated to organic ligands to form one, two, or three dimensional structures) [16-20]

Uses

- In lab often used to facilitate contaminant-free exchange of gases. Mold spores, bacteria, and other airborne contaminants will become trapped, while allowing gases to pass through the material. This allows for a sterile environment in the contained area.
- Microporous adhesive tape (surgical tape) was introduced in 1959 with the trade name *Micropore.* It can be used to hold gauze padding over small wounds, usually as a temporary measure until a suitable dressing is applied.
- Microporous tape is used by some professional extreme yo-yoers to wrap around their fingers and prevent string burn or irritation.
- Rock climbers use microporous tape to wrap their hands in ‘tape gloves’, a means of protecting the skin from rock abrasion
- Microporous tape is also used by some film and TV sound recordists to affix small radio microphones to actor’s skin.
- Microporous material is also used as high performance insulation material used from home applications up to metal furnaces requiring material that can withstand more than 1000 Celsius.

Mesoporous Materials (2-50nm)

- Typical mesoporous materials include some kinds of silica and alumina that have similarly-sized fine mesopores.
- Mesoporous oxides of niobium, tantalum, titanium, zirconium, cerium and tin have also been reported.

- A mesoporous material can be disordered or ordered in a mesostructure.
- Mesoporous silica is the polymeric form of silica formed by Tetraethyl orthosilicate (which is a monomer unit)

Examples of prospective applications

1. Catalysis (as greater pore size is offered), sorption (both adsorption and absorption)
2. Gas sensing
3. Ion exchange (exchange of ions between two electrolytes or between an electrolyte solution and a complex)
4. Optics (including its interactions with matter and the construction of instruments that use or detect it)
5. Photovoltaics (conversion of light into electricity using semiconducting materials like in solar panels)

Macroporous Material (>50nm)

- Pores of size more than 50nm host preferential soil solution flow and rapid transport of solutes and colloids.
- Macropores increase the hydraulic conductivity of soil, allowing water to infiltrate and drain quickly.
- In soil, macropores are created by plant roots, soil cracks, soil fauna, and by aggregation of soil particles into peds (soil granular structure).

Properties and characterization of nanoporous materials

Nanoporous materials are porous material which is a material containing pores (voids). Nanoporous materials are organic (or) inorganic framework which have large porosities greater than 0.4 nm and pore diameter of 1-100 nm. The skeletal portion of the material is often called matrix (or) frame and the pores which are filled with liquid (or) gases.

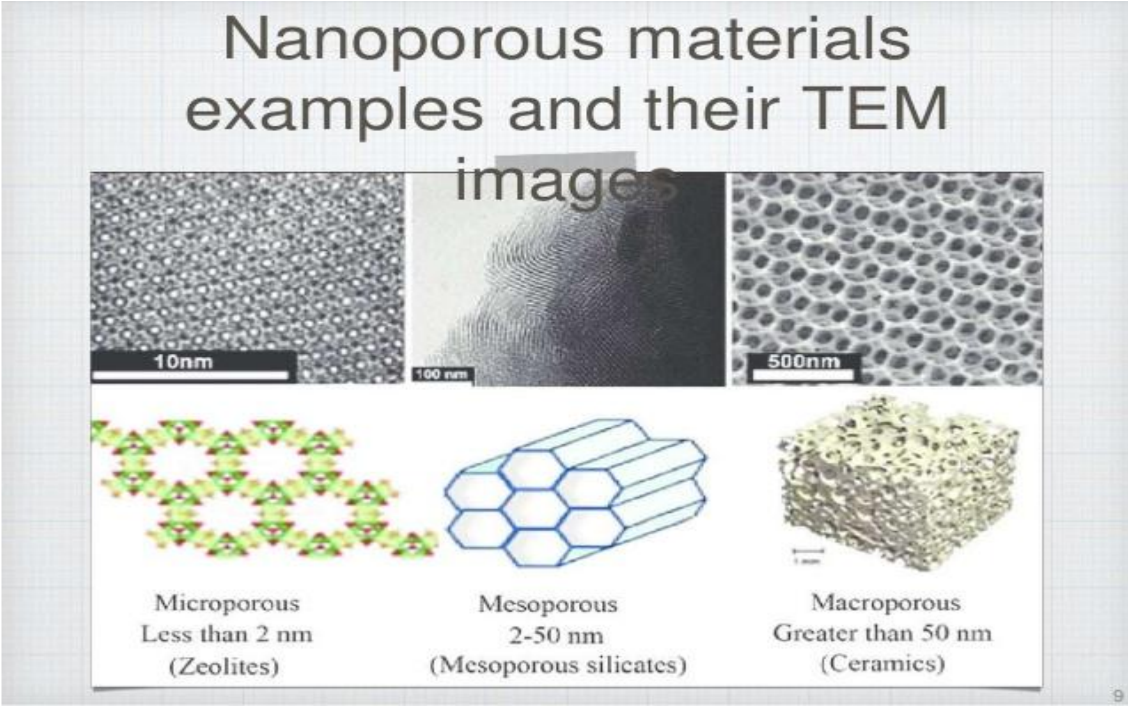
Nanoporous materials have high surface to volume ratio, with a high surface are and large porosity and ordered uniform pore structure. They can be used for many applications such as catalysis, separation and sensing. Inorganic nanoporous materials made of oxide are non toxic, inert and chemically and thermally stable.

Polymer and ceramic based non porous materials are readily available but it is tough to produce metal Nanoporous materials. They have a very large pore volume (upto 70%) and very high surface area (>700m^2/g).

One method of doing so is to combine polymers with different melting points, so that upon heating one polymer degrades. A nanoporous material with consistently sized pores has the property of letting only certain substances to pass through, while blocking others.

CLASSIFICATION OF NANOPOROUS MATERIALS

	Polymeric	Carbon	Glass	Alumino-silicate	Oxides	Metal
Pore Size	Meso-Macro	Micro-meso	Meso-macro	Micro-meso	Micro-meso	Meso-macro
Surface area/Porosity	Low>0.6	High 0.3-0.6	Low 0.3-0.6	High 0.3-0.7	Medium 0.3-0.6	Low 0.1-0.7
Permeability	Low-medium	Low-medium	High	Low	Low-medium	High
Strength	Medium	Low	Strong	Weak	Weak-medium	Strong
Thermal stability	Low	High	Good	Medium-high	Medium-high	High
Chemical stability	Low-medium	High	High	High	Very high	High
Costs	Low	High	High	Low-medium	Medium	Medium
Life	Short	Long	Long	Long	Medium-Long	Long



Techniques for characterization of nanoporous materials

Crystalline structure

- Single crystal and powder X-Ray diffraction (XRD)
- Electron Crystallography

Oxidation state and co ordination

- X-Ray Absorption spectra
- X-Ray Photoelectron spectra (XPS)
- UV-Visible spectra
- Solid state NMR (mainly co ordination)

1. Elemental Analysis – ICP-AES, XPS
2. Surface area and pore size – N_2 adsorption-desorption isotherm
3. Morphology - SEM
4. Pore structure – TEM

APPLICATIONS OF NANOPOROUS MATERIALS

Catalysis

Heterogeneous catalysis has had a major impact on chemical and fuel production. More efficient catalytic processes are required to improve catalytic activity and selectivity. Therefore tailor designs of catalytic materials with desired microstructures are needed. Nanoporous materials will be used because of their large and accessible surface area of the catalyst. Nanoporous metals have high surface areas, low specific densities and rich surface chemistry and are highly efficient electro catalysts for the oxidation of small organic molecules e.g. methanol, ethanol and formic acid.

Environmental separations

As the regulatory limits on environmental emissions become more strict industries have developed separation technologies that remove contaminants and pollutants from waste gas and water streams. Adsorption processes and membrane separations are the two dominant technologies. Adsorbent materials and membranes are being applied and new adsorbent membranes are invented for environmental applications that remove sodium oxide nitrogen oxide and VOCs emissions. Adsorbents of traditional types such as carbons, zeolites, silica gel and activated alumina.

Clean Energy Production and Storage

Future energy supply will be dependent on hydrogen as a clean energy carrier. Hydrogen can be produced from fossil fuels, water electrolysis and biomass. Key to the process of cost effective conversion of coal to hydrogen and carbon capture is nanoporous material catalysts. Nanoporous material will be important in this process, nanomaterials such as carbon nanotubes show great promise of being the future catalysts in these fuel cells.

Sensors and actuators

Nanoparticles and nanoporous materials possess large surface areas and high sensitivity to slight changes in environment. These materials are widely used as sensor and actuator materials. Gas sensors sensitivity is dependent on surface areas and gas sensors based on nanoporous metals such as titanium oxide or zinc oxide are being developed and applied to detectors of combustible gases. Gas sensors rely on the detection of electric resistivity change upon change in gas concentration and their sensitivity is dependent on surface area.

Biological applications

Nanomaterials are assembled and structured on the nanometer scale and are attractive for biotechnology applications because they can be used for their material topography and spatial distribution of functional groups to control proteins, cells and tissue interactions and for bioseperation. Nanoporous materials are often bio-compatible afford the capability to build enzymatic nanomaterials that mimic biological reactions. Immobilizing enzymes onto nanoporous materials can be used for biological reactors to produce drugs, decontaminate waste etc. Nanoporous material can be used for biosensors. Piezoelectric biosensors utilizing high surface area nanoporous coatings have increased sensitivity in detection.

Cell Culture

Porous silicon has revealed to be convenient cell culture platforms for the growth of cells such as mammalian cells, neuronal cells, lens cells etc. Substrate topography affects cell functions such as adhesion, proliferation, migration and differentiation. The controllable and tunable pore size and structure of silicon allows for substrates for the proliferation and adhesion of cells.

Drug Delivery

Porous silicon is suitable material for drug delivery due to its high porosity and high surface area. Therapeutic agents have been loaded into porous silicon pores such as small molecules such as doxorubicin. For drug delivery applications several aspects must be considered such as the pore size since the molecule must be smaller than a pore diameter to penetrate into the pores. Porosity is important since the quantity of the drug loaded into the pores is related to capacity of pores.

Templates

Using porous silicon as a template provides the means for construction of complex structures. Porous silicon is an appropriate template because it can be fabricated with high precision and uniformity and porosity pore size and pore depth can be tuned by adjusting the electrochemical preparation techniques. Fibers, tubes or porous layers of several materials are fabricated by replicating the porous silicon structure. This template assisted technique has advantage of readily create large area and ordered arrays of micro and nanostructures with control over structural parameter.

Nanoporous Materials Based Sensors for Pollutant Detection

Nanoporous-based materials recently have attracted considerable attention in sensing because of their great surface-to-volume ratios, outstanding chemical and physical properties. Nanoporous-based materials have been used for the detection of trace metals and organic by sensing.

- Nanoporous materials are also of scientific and technological importance because of their ability to absorb and co operate with atoms, ions and molecules on their sizeable interior surfaces and pore space.
- Adsorbents and Ion exchange
- Nano-reactor (quantum lines and dots, engineering polymers)
- Guest-Host interaction (immobilized homogeneous catalysts, enzymes, nonlinear optics)
- Low dielectric constant mediate

Zeolite

- Inorganic porous material with silicon and aluminium with a multidimensional and interconnected pore system.
- Because of nano and micro scaled pores, they have large inner surface area.
- 0.3-1 nm in diameter.
- Pore volume: 0.1-0.35 cc/g.

Preparation Depends on

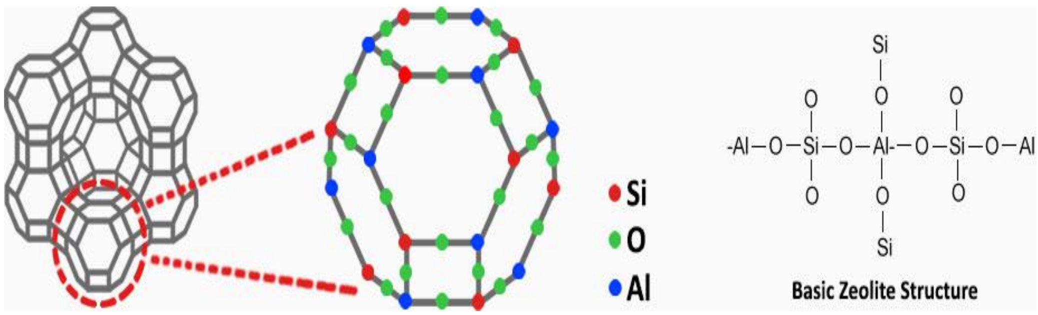
1. The Reagent type

2. The addition order
3. The degree of mixing
4. The crystallization temperature
5. Time
6. Composition of the sources

*Numerous organic-inorganic interactions occur during synthesis process.

APPLICATIONS

- Catalyst in chemical processes.
- Ion exchanger or water softener in detergents.
- Filter for desulphurization in flue gases.
- Used in removal or reduction of carbon dioxide system in International Space Station.
- Solar thermal collector for adsorption refrigeration.



Aerogel

- Synthetic porous ultralight material derived from a gel
- Have a porous solid network with 99.9% air in its pockets.
- Translucent in nature, weights three times that of air.
- Three types of aerogels:

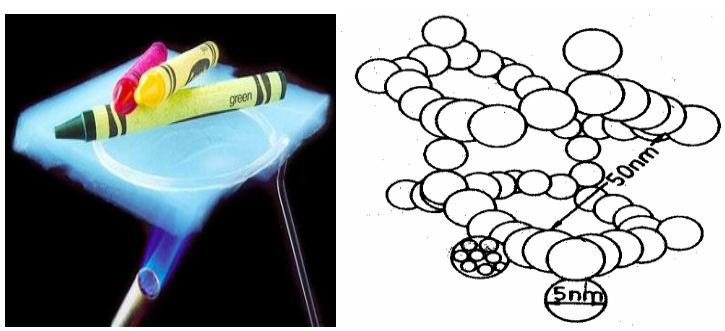
1) Silica Aerogels
2) Carbon Aerogels
3) Metal oxide Aerogels

Preparation by Sol-Gel Method

- Wet gels are aged for certain periods of time to strengthen the gel network, and then brought to temperature and pressure above the solvent critical point in autoclave.
- The solvent is removed from gel network.
- Highly porous structure of the gel network is obtained.
  (pore volume =99%, surface area > 1000m^2/g)

APPLICATIONS

- Thickening agents in paints and cosmetics
- Collector of space dust particles by NASA in ISS
- Catalyst
- Precursors
- Water Purifiers
- Super capacitors
- Racquets for tennis, squash or badminton



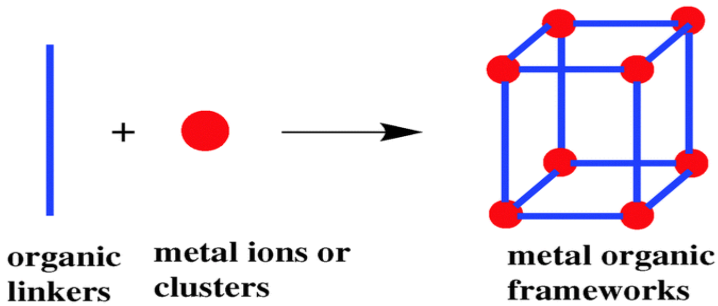
Structure of Aerogel

METAL ORGANIC FRAMEWORK

- Porous compounds consisting of clusters or metal ions coordinated with organic complex
- Can be 1/2/3 dimensional structure
- Sensitive of air and moisture
- Can trap carbon because of small, tunable pore sizes and high void fractions.

APPLICATIONS

- Gas Separation
- Catalysis
- Hydrogen storage
- Gas adsorption
- Gas Purifications
- Ion-Exchange
- Sensor Materials
- Bio-Medical Applications



CONCLUSION

Nanoporous materials are an important material that has applications in many areas including biomedical, catalysis and green energy. Almost all zeolites and their derivatives are microporous whereas the aerogels are mesoporous materials. Nanoporous materials have high surface area, tunable pore sizes, and high surface to volume ratio and can be functionalized. They have been used to create drugs for cancer, catalysis of reactions due to its high surface area, capturing hydrogen and carbon into its pores and surface, platforms for cell culture and other numerous applications.

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