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REVIEW ARTICLE OPEN ACCESS

Surface Engineered New Approach for Mesoporous Alumina and Nanoparticles - A Review

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ABSTRACT
Mesoporous materials have been widely used in redesigning pharmaceutical formulations for determination of its pharmacokinetic characteristics. They have demonstrated great advantages in providing well controlled surface area, pore size, pore volume and have become notice in distinct fields counting electronics, separation, catalysis etc. Compared with microporous materials, they present improvement in molecular mass transfer thus allowing larger reactant molecules involved in the reaction systems. Our major emphasis is to give a centred around information about factors influencing the characteristics of mesoporous material and most preferred method of choice for the synthesis of mesoporous material .
***Keyword :** Mesoporous, Pore size, Sol-gel, Synthesis, Mechanism*

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INTRODUCTION

Emerging research interest has been devoted to the field of mesoporous inorganic nanoparticle synthesis. Inorganic nanoparticles can be interpret as particles of metal oxide or metallic composition possessing at least one length scale in the nanometer range. The mesoporous structure offers increased surface area as a result of its intricate and structured network of pores. The preparation of mesoporous alumina (MpAl) with high surface area a uniform pore structure and narrow pore size distribution is of great interest for both technological applications as well as fundamental research. MpAl is superior to mesoporous silica (MpSi) because of its high hydrolytic stability along with a different point of zero charge which makes it suitable platform for loading different metal species. The performance of conventional MpAl however, is limited because of its uncontrolled porosity and deactivation by choking and plugging that hinders the diffusion of reactants and products.According to the International Union of Pure and Applied Chemistry (IUPAC) rules, pores are classified as micropores when their diameter d is in the range of 0.2–2 nm, mesopores when 2 nm $<d<$ 50 nm, or macropores when d > 50 nm. Porous alumina, owing to their thermal, chemical, mechanical stability and low cost are extensively used in catalysis, adsorption, and separation.[1,2] In general the control of pore geometry and size is crucial to adjust their performance in these applications especially in case rely on size or shape selectivity.Porous alumina is most vital engineering material extensively used in catalysis, adsorption, and separation. Traditionally, transition alumina or activated alumina has been used as porous alumina, but there is a problem of deactivation in catalysis by pore plugging due to coke formation in micropores.[3] Therefore, it is desirable to have alumina with mesopores in narrow size distribution. Thus, the synthesis of mesoporous alumina with controlled porosity and high thermal stability has been actively pursued. With the advent of mesoporous materials the synthesis of mesoporous alumina with high surface area and narrow pore size distribution is promising for application enhancement of porous alumina.[4].

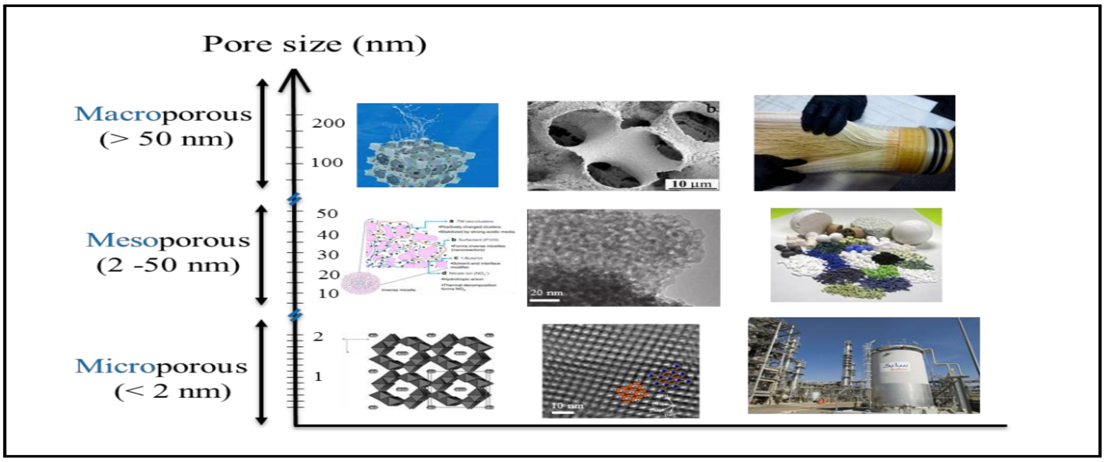

Fig. 1. Schematic diagram, electron microscopy images, and applications of microporous, mesoporous and macroporous materials [5,6].

Mesoporous nanoparticles has solid framework with porous structure and large surface area which allows the attachment of different functional group for targeted drug moiety to a particular site. Chemically, MSNs have honeycomb like structure and active surface. Active surface enables functionalization to modify surface properties and link therapeutic molecules. The mesoporous form of silica has unique properties particularly in loading of therapeutic agents at high quantities and in the subsequent releases. Due to strong Si-O bond silica based mesoporous nanoparticles are more stable to external response such as degradation and mechanical stress as compared to niosomes, liposomes, and dendrimers which inhibit the need of any external stabilization in the synthesis of MSNs.[5,6]Another distinctive advantage of MSNs is that they have well defined surface properties that allow easy functionalization of silanol containing surface to control drug loading and release. Mesoporous silica nanoparticles due to their low toxicity and high drug loading capacity used in controlled and targeteddrug delivery system. Basically silica is widely present in environment comparison to other metal oxides like titanium and iron oxides it has comparatively better biocompatibility.In the present era not too many new chemical entities are coming in market primarily due to the fact that either they have poor solubility or incomplete absorption.[7-8] Various methodologies have been explored to overcome this issue but none of them possess all the prerequisites. At present time nanochemistry becomes one of the main growing directions of nanoscience. Frequently, nanometer-size metallic particle shows unique and considerably changed physical, chemical and biological properties compared to their macro scaled counterparts, due to their high surface to volume ratio. Thus these mesoporous nanoparticles have been the subject of substantial research in recent years.[9]

The Advantages of Mesoporous Materials

a) The mesoporous material shows affinity towards adsorption of small molecules due to highly ordered and controllable size.
b) Due to high surface area and large pore volume results in adsorption of large no of reactants.
c) Mesoporous material includes various oxides like silica, alumina and metal oxides. The transition metal oxide has its own importance among non silica mesoporous materials because they possess d-shell electrons confined to nanosized walls, redox active internal surface, and connected pore network.
d) Mesoporous materials are thermally stable, chemically stable, biocompatible and have low toxicity.[10]

Importance of the Project

e) Due to lack of specification and solubility of drug molecules patients have to take high doses of drug to achieve desired therapeutic effects for the treatment of diseases. To solve these problems there are various drug carriers present in pharmaceuticals which can used to deliver therapeutic agents to target site in the body. Mesoporous silica materials become known as a promising candidate that can overcome above problems and produce effects in controllable and sustainable manner.
f) Due to numerous applicability of mesoporous material in different chemical investigation it has been extensively investigated for years. Due to immanent belonging of aluminum oxide such as high melting point, low thermal conductivity, chemical inertness and corrosion resistance have made alumina of use to many different industrial and technical processes. Among these γ-Al_2O_3attend

exceptional properties as good thermal and chemical stability, high specific surface area and surface with proportion and distribution of chemical active centred. Sol-gel technique has proved particularly efficient in producing samples with such characteristics. This technique consists of hydrolysis aluminium alcoxide to a suspension that after peptising becomes a colloidal suspension or sol by evaporation turns into gel and after calcination into a metal oxide. The porous structure of material derived from this method is highly dependent on the preparation and calcination parameters and to the incorporation of additives. Thus these alumina can be used as carrier for delivering and controlling release of poorly water soluble drug.

g) The reason why these nanoparticles (NPs) are attractive for medical purposes is based on their important and unique features such as their surface to mass ratio that is much larger than that of other particles their quantum properties and their ability to absorb and carry other compounds such as drugs, probes and proteins. The pharmaceutical formulations and the manufacturing processes associated with them are quite complex because they involve a large number of manufacturing variables

FACTORS INFLUENCING THE CHARACTERISTICS OF THE MESOPOROUS ALUMINA

Pore Size

One of the most concerned question raised how drug is incorporated to mesoporous materials it can be accomplished by soaking of the matrix in a highly concentrated drug solution and subsequent drying. According to proceedings the most process is based on the adsorptive properties of mesoporous materials. The pore size of mesoporous materials determines the size of molecule that can be adsorbed into the mesopores. Thus the adsorption mechanism of molecules in the mesoporous matrix is supervised by size selectivity. Commonly pore diameters slightly larger than the drug molecule dimensions(pore/drug size ratio>1) are enough to allowadsorption of drug inside the pores. One of the most important characteristics of mesoporous materials is that the mesopores diameters can be tuned from 1.5 nm to several tens of nanometres by changing the chain length of surfactant employing polymeric structure directing agents or solubilizing auxiliary substances into micelles.[11]These different tools allow mesoporous matrices to be tailored to host either small molecules or macromolecules such as proteins.

Surface Area

As mentioned above the drug loading process is mainly based on adsorptive properties of mesoporous materials. Therefore the surface becomes the most determining factor for the amount of adsorbed drug. In general terms it is convenient to host large amounts of pharmaceuticals or at least to have the choice of incorporating high or low doses of a drug into the matrix. This challenge can be tackled by two different approaches by increasing and reducing the surface area or by modifying the surface drug affinity. The first approach involves the amount of surface available for drug molecules. So long as the pore size allows the drug to get into the matrix the higher the surface area higher the amount of drug adsorbed. The final drug content can be very sensitive to the surface area S_{BET}.[12]

Pore Volume

The surface area and pore diameter are critical factors for drug adsorption and release in implantable ceramic-based drug delivery systems. The outermost mesopore surface of virtually insoluble porous frameworks is responsible for interaction with loaded drug. As the pore size is usually less than 15 nm and surface areas are roughly1000 m^2/g the pore volumes are generally in the range of2.0 cm^3/g. The drug mesopore interaction is a surface phenomenon however weak drug-drug interactions can result under loading conditions and could lead to pore filling. In this case, the pore volume is a key factor in determining the amount of drug adsorbed. It was recently reported that several consecutive loadings of drug in ordered mesoporous materials leads to larger filling of mesopores which was attributed to increased drug intermolecular interactions within the pore voids, whereby larger pore volumes may result in greater drug loading.

FUNCTIONALIZATION OF MESOPOROUS DRUG-DELIVERY SYSTEMS

The keystone in the development of silica mesoporous materials as drug delivery systems is modification or functionalization of surface through organic groups. This process provides numerous possibilities to control drug adsorption and release. Mesoporous silica shows a high density of silanol groups which can be used to obtain functionalized surfaces by grafting organic silanes ($(RO)_3SiR$). The drug release can be effectively controlled by different methods the most developed of which is increasing the drug surface interaction. For this purpose the surface is functionalized with chemical groups that are able to link to the drug molecules through ionic bonds or through ester groups.

GENERAL SYNTHESIS APPROACH FOR MESOPOROUS MATERIALS

Generally, the approaches to synthesize mesoporous transition metal oxide can be classified into two methods the hard template method and soft template method. The fabrication process includes reinforced crystallization, post-synthesis solid-solid conversion, and nanocasting. The inorganic precursor is firstly filled in pores of hard template and then it converted to inorganic solid network. After the network is formed hard template is removed. The obtained material is actually a replica of hard template. The disadvantage of hard template method is that the template is difficult to remove. In the soft template method surfactants are used as templates. This fabrication process is an evaporation induced self assembly process. The inorganic precursor and the surfactant are firstly mixed forming a wet gel in solvent. Then a mesoporous network is formed from the inorganic precursor. Further surfactant is removed by calcination or solvent extraction.[13]

SOL-GEL PROCESS FOR SYNTHESIS OF MESOPOROUS ALUMINA

The rapid development of sol-gel techniques during the past two decades has led to fast progress in the deliberate synthesis of porous materials. These techniques complement a broad range of conventional procedures used for the preparation of amorphous solids or glasses such as precipitation or impregnation methods followed by high temperature treatments. Sol-gel methods represent an attractive and easy to tailor alternative to conventional synthesis method. Compared to solid-state reactions, this mild synthesis method usually results in the formation of mixed oxides of improved homogeneity. The sol-gel process itself is low cost requires only mild reaction conditions and provides homogeneous gels with most elements of periodic table that are capable of solid oxide formation. Amorphous oxides are formed by sol-gel processes in a polycondensation reaction under kinetically controlled reaction conditions. The choice of reagents, additives, reaction and drying conditions allows for the control of pore structure and porosity, composition, surface polarity, surface acidity, and crystallinity. Sol-gel processes allow for a relatively facile tailoring of morphology and mixed oxides to the desired application. Pore volume, porosity, specific surface area, and surface acidity are typical parameters that can be tailored. The sol-gel process is generally classified as a soft template method. During the sol-gel process, an oxide network is formed through poly-condensation of inorganic precursors in the liquid. Depending on the synthesis procedure, the morphology of material synthesized by sol-gel process varies. In this study, powder form mesoporous materials were synthesized through the steps of hydrolysis, condensation, gelation, evaporation and heating. Usually in the sol-gel process, micelles, which have hydrophobic tails of surfactants inside and hydrophilic tails of surfactants outside are formed in water medium, usually resulting in metal oxide materials of amorphous wall structure and disordered pore system. In order to obtain crystalline wall and monomodal pore size distribution, inverse micelles, which have hydrophobic tails of surfactants outside and hydrophilic tails of surfactants inside to form in organic solvent medium.[14]

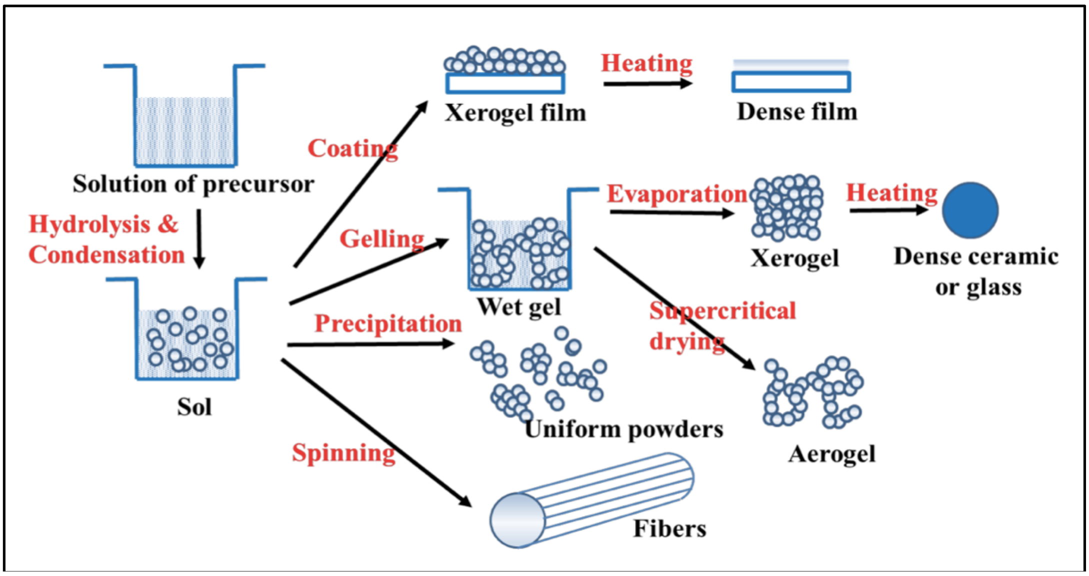

Fig. 2. Various steps in the sol-gel process to control the final morphology of materials [15].

MECHANISM OF SOL-GEL BASED METHOD FOR SYNTHESIS OF MESOPOROUS ALUMINA

Generally, the sol-gel based inverse micelle method includes three steps, the solution step, the sol-gel transition step, and the post synthesis step (Fig. 2). In the solution step inorganic precursor solution is formed. The type of inorganic precursors, surfactant properties(such as size, type, mixing ratio), and small additional molecules can be used to tune different properties of mesoporous materials. In the sol-gel transition step the solvent starts evaporating and then the micelles come together. When the solvent is totally dried, the inorganic precursors change into oxide and then oxide network. In this process, reaction temperature, reaction time, and solvent are key factors that affect the properties of mesoporous materials. In the post synthesis step the surfactant is first extracted by solvent and thereafter products are generated during the sol-gel transition step such as NO_X and carboxyl groups are removed by calcination at 150°C. During post synthesis calcination temperature, heating rate, and atmosphere can be adjusted for tuning the properties of mesoporous materials. Further modification, such as sulfurization, reduction, and oxidation allow the generation of mesoporous metal sulphides, metal oxide with mixed valence, and metal oxide with different phases.[15]

SURFACE MODIFICATION OF THE MESOPOROUS ALUMINA

A second aspect for modifying nanoparticles is to render them compatible with another phase. For example, metal particles can be made water soluble when appropriate groups are attached. Another example is use of modified inorganic (nano)fillers in organic polymers. The modification can avoid homogeneity and compatibility problems between the two phases and thus improve the mechanical properties of composite. A third interest in nanoparticles modification is to enable their self organization. A relatively unexploited additional possibility is the functionalization through organic groups. While simple organic groups are sufficient to protect mesoporous particles against agglomeration.The functional organic groups on the particle surface may allow deliberate interaction of nanoparticle with molecules, other particle, surfaces, or solids. The mentioned possibilities are synergetic. For example, surface functionalities also protect the mesoporous particles against agglomeration and may be required to enable their self-organization. For example, the surface modification of alumina will allow the attachment of drug moiety to mesoporous alumina.

CONCLUSION

Recently the large no of researchers focused on the new emerging trend by utilizing various size and shapes of mesoporous alumina having numerous applications. Hence due to this strategies to develop controlled shapes have only been develop. Therefore we comment that the mesoporous material showing more potential in the field of nonmaterial science showing opening of various opportunities.

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