

Volume

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MATERIALS SCIENCE  
AND TECHNOLOGIES

Mahmood Aliofkhazraei  
Editor

# Comprehensive Guide for Mesoporous Materials

Synthesis and Characterization

NOVA

MATERIALS SCIENCE AND TECHNOLOGIES

**COMPREHENSIVE GUIDE FOR  
MESOPOROUS MATERIALS**

**VOLUME 1**

**SYNTHESIS AND CHARACTERIZATION**

MAHMOOD ALIOFKHAZRAEI  
EDITOR



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MESOPOROUS MATERIALS**

**VOLUME 1**

**SYNTHESIS AND CHARACTERIZATION**

# **MATERIALS SCIENCE AND TECHNOLOGIES**

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## PREFACE

This is the first volume of the four volume set of Comprehensive Guide for Mesoporous Materials. The discovery and application of mesoporous materials in the different industries, including the catalyst industry, is one of the major advances over the past two decades. One of the important mesoporous materials is zeolite. Over the past decade, different types of zeolites have been produced in the nanometer range dimensions. Porosities can also be regular or irregular. Due to more research done on mesoporous materials, knowledge of this science has increased. Researchers are now able to make mesoporous materials with dimensions equal to the predetermined requirements to use in engineering, such as with molecular separation membranes.

This volume mainly discusses the synthesis and characterization of mesoporous materials. Some of the mesoporous materials discussed in this volume are alumina, carbon, silica and also polymeric materials. There are 15 chapters in this volume; each one includes examples of these interesting materials, supported by appropriate figures for better clarification.

Chapter 1 - The synthesis of mesoporous alumina has a very interesting area of application, particularly as catalyst or catalyst support. This chapter focuses on the individual synthesis routes to produce mesoporous aluminas with large surface areas and narrow pore size distributions. The utilization of various structure-directing agents (cationic, anionic and neutral) during the preparation of aluminas was studied. The syntheses carried out with aqueous ionic surfactants produced aluminas with poorer textural properties than the aluminas prepared with nonionic methods in alcoholic solutions. It was found that textural properties of the aluminas differ depending on the preparation method. Some catalytic applications of mesoporous aluminas were cited. It was found that the stages of precipitation, aging and elimination of the surfactant, required more detailed experimental information.

Chapter 2 - The process of cationic layered minerals intercalation with inorganic pillars leading to PILC and PCH materials was presented and discussed. PILCs are relatively well known group of clay-based materials, thus authors concentrated mainly on presentation of PCHs (Porous Clay Heterostructures), which are a relatively new group of porous materials that can be obtained from layered clay minerals by a surfactant directed method. PCHs are characterized by the combined micro-mesoporous structure, relatively high surface area, high thermal and hydrothermal stability, surface acidity and ion-exchange properties and therefore, these materials are very promising for application in various processes, including

catalysis and adsorption. The synthesis of PCHs and their application in various catalytic and adsorption processes is presented and discussed.

Chapter 3 - This chapter describes the preparation and surface modification of mesoporous films and membranes based on silica colloidal spheres. Silica spheres form close-packed fcc lattice with ordered arrays of interconnected mesopores upon vertical deposition from colloidal solutions. Silica colloidal films can be prepared on various solid supports and suspended in glass or silicon support. Free-standing silica colloidal membranes can be obtained by sintering above 1000 °C. Silica colloidal membranes have a highly ordered geometry; they are capable of size-selective transport and can be surface-modified in a well-defined and controlled manner with small molecules and polymers. The surface modification can be achieved using silanol chemistry, and polymer brushes with narrow mass distribution and controlled length can be formed on the mesopore surface using atom transfer radical polymerization and ring-opening polymerization. The transport in the resulting mesoporous membranes can be controlled by pH and ionic strength, temperature, light, and small molecule binding. Proton conducting silica colloidal membranes can be prepared by filling the mesopores with sulfonated polymer brushes.

Chapter 4 - The development of new materials, such as those based on mesoporous structures involved in green processes, is a current and hot issue with special relevance on the design of novel, more efficient and environmental-friendly catalysts. In fact, in the last decade, the number of reported novel mesoporous materials with application in catalysis has been notably increased.

In this sense, this chapter is intended as an update of catalytic processes of interest involving mesoporous materials such as functionalized mesoporous silicates and metallosilicates, metal-organic-frameworks and mesoporous carbons. This overview covers the most recent achievements in the application of mesoporous structures as catalysts and even as catalyst supports in acid-base reactions related to Fine Chemistry.

Chapter 5 - Owing to the unique physicochemical and electric properties the ordered mesoporous carbons have been a subject of intense research for many years. They have a well-developed surface area and great pore volume and have been found suitable for a number of applications including catalysis, energy storage and transformation, nanotechnology and as adsorbents in processes of air, water and industrial gas purification.

This chapter presents a survey of methods for the synthesis of mesoporous carbons with particular emphasis on the hard- and soft-template methods. The factors influencing the ordering as well as textural and structural parameters of ordered mesoporous carbons are identified and discussed such as the physicochemical properties of these materials, the so far applied methods of their modification and their potential use as adsorbents of various compounds from the liquid phase, including amino acids, vitamins and dyes.

Chapter 6 - Nickel ion-loaded mesoporous silica (Ni-M41) was found to show good activity for one-step conversion of ethene or ethanol to propene by us. The conversion of ethene was 68% and the propene selectivity was 48% in a continuous gas-flow reaction at 673 K. The following reaction scheme was suggested based on the partial pressure dependences and the reactions of the intermediate compounds: dimerization of ethene to 1-butene, isomerization of 1-butene to 2-butene, and metathesis of 2-butene and ethene to propene. Various physicochemical techniques were applied to study the nickel species loaded on M41 and elucidated the formation of 2:1 nickel phyllosilicate-like species and the existence of three-coordinated  $\text{Ni}^{2+}$  ions on five-membered Si-O rings, which were

suggested as active sites for the dimerization reaction of ethene. The conversion of ethanol on Ni-M41 was finally introduced and the reaction mechanisms were discussed. Two routes from ethanol to propene were suggested; the dehydration route and the dehydrogenation route. All of the results indicate that the formation of propene from ethene or ethanol could be achieved without using the shape selectivity well known in zeolite catalysis.

Chapter 7 - Over the last decades, nanoporous polymeric materials have been the subject of widespread interest and intense research as they can arguably be considered for nanotechnological applications, e.g., advanced nanofiltration membranes, interlayer dielectrics, high surface area catalytic supports, as well as size/shape-selective nanoreactors. Organic porous materials have unique properties that distinguish them from their inorganic nanostructured analogues, such as tunable mechanical properties, ease to be functionalized, and especially lower production cost. Designing nanoporous polymeric materials with controlled morphology and functionality thus constitutes an active research area. In this context, original approaches using suitable porogen templates have emerged: such templates are able to induce specific structural pores within the residual frameworks. These template-oriented routes are very interesting as a wide array of nanoporous polymers with a well-defined porosity can be derived from miscellaneous macromolecular architectures. Smart methodologies include molecular imprinting, selective removal of a porogen homogeneously blended within a thermostable matrix, selective removal of one partner from (semi-)interpenetrating polymer networks, selective destruction of one block in self-organized block copolymers, as well as removal of self-assembled molecules from supramolecular architectures. This chapter affords a critically selected appraisal of these synthetic strategies developed to create functional nanoporous polymers and investigates the scope and limitations associated with the utilization of such routes.

Chapter 8 - In the synthesis of mesoporous materials, there is a high interest to find simple, efficient and rapid processing methods. Over the last decade, UV irradiation has made a valuable contribution in this field especially for mesoporous silica films. Initially implemented to eliminate the organic template by photodegradation, this technology has proven its utility for patterning, driving sol-gel polymerization and controlling self-assembly. Most photo-mediated processes rely on in situ photogeneration of Brønsted photoacids to promote hydrolysis and condensation of siloxane species. Many advantages can result from a light-induced polymerization as regard to efficiency (yields, reactivity), environmental impact (solvent-free, low energy consumption) and improved control (temporal and spatial control). This chapter provides for the first time a state-of-the-art and comprehensive review of domains in which light has enabled technical innovations in the synthesis of mesoporous inorganic films.

Chapter 9 - Mesoporous undoped and metal (Fe or Cu) doped carbon aerogels obtained using a sol-gel process, followed by low temperature supercritical drying and various pyrolysis conditions were synthesized. The resulting materials were characterized by means of elemental analysis, nitrogen adsorption-desorption, TEM, SEM, AFM and XRD methods. The presence of graphene-like structures was evidenced in the case of Fe-doped carbon aerogels. Due to their special morpho-structural properties: high surface area and pore volume, narrow mesopore size distribution, low density, etc., these materials were tested in different applications such as: phenol chemical wet air oxidation and phenol and pesticide adsorption from aqueous solutions.



Chapter 10 - Organic porous materials are a class of advanced materials, which have shown promising potential in many technological applications. Polyaniline (a conducting polymer) is a novel organic semiconducting material, which has attracted considerable attention because of its remarkable optical, electrochemical, and conducting properties. Nanostructured polyaniline combines the properties of low-dimensional organic conductors with high surface area materials. Polyaniline has been investigated in a number of catalytic and bio-technological applications because of the unique flexibility with respect to morphological controlled synthesis, tunable pore size, and ion-exchange properties. This chapter covers the state-of-the-art in the synthesis, chemical structure and properties, and electrocatalytic activity of polyaniline for sensing application. Single and simultaneous detection of clinically and pharmaceutically important molecules using polyaniline based electrodes is discussed in detail.

Chapter 11 - Self-assembly of colloidal particles at liquid/liquid interfaces leads to the formation of mesoporous shells: Pickering emulsions result from assembly at interface between immiscible hydrophilic/hydrophobic phases, while shells separating an aqueous core from an aqueous continuous phase give rise to 'colloidosomes'. In both cases, the unique properties of the mesoporous shells provide selective and/or controlled release with unique transport properties. This chapter reviews the characteristics and properties of colloidal assembly at the interfaces of Pickering emulsions and colloidosomes, and the factors controlling transport through the colloidal shells.

Chapter 12 - The development of materials with potential application in CO<sub>2</sub> capture is a topic of scientific interest. In this respect it was established that by adding nitrogen groups is achieved increasing adsorption of this gas. Chemical modification was performed in gas phase with ammonia and ammonium hydroxide solution at 30%, of various activated carbon monoliths obtained by activation of African palm stone with H<sub>3</sub>PO<sub>4</sub>, ZnCl<sub>2</sub> and CaCl<sub>2</sub> solutions. The original and modified monoliths were characterized by N<sub>2</sub> adsorption at 77K, infrared spectroscopy, Boehm titration and immersion calorimetry in benzene and water. Was evaluated the ability of CO<sub>2</sub> adsorption in a volumetric equipment at a temperature of 273 K and until 1 bar, was obtained values between 120-334 mgCO<sub>2</sub>g<sup>-1</sup>. The experimental results indicated that through both methods of chemical modification used in this work, is achieved the increasing the content of nitrogen groups in the monolith and thus increases the CO<sub>2</sub> adsorption capacity.

Chapter 13 - X-ray scattering is a very important tool for the investigation of mesoporous materials. In this chapter, the authors gave an overview of their use for the study of periodic porous networks. First, the authors introduced the three types of textures: monoliths, powders and thin films. Then the authors reviewed all the known possible structures encountered for mesoporous materials. The basic notions of X-ray scattering are explained: diffraction, reciprocal space and space-group determination. They are detailed for the different types of structures: 2D or 3D networks, monolith, powders and thin films. More advanced analysis methods based on the measurement of the Bragg peaks intensities in relationship with the form factor contribution are introduced, allowing to a refined structural description of the porosity. Lastly, some examples of in-situ studies under controlled atmosphere or during material formation are given. These examples illustrate the wide range of experimental possibilities offered by X-ray scattering analysis.

Chapter 14 - The reaction of resorcinol and formaldehyde, catalyzed by base, produce a porous gel formed by chain-like aggregates of resin nanoparticles. Conventional drying

caused aggregation of the constituent nanoparticles, with collapse of the pores, producing a resin without open pores (xerogel). The pyrolysis of the resin produces a compact carbon. The usual way to avoid pore collapse is to avoid water evaporation and instead drying using supercritical fluids (aerogels), lyophilization (cryogels) or using low surface tension solvents (ambigels). In all cases, the procedures are complex and expensive, including solvent exchange and/or long curing steps. In this chapter the authors describe the use of different species (micelles, polyelectrolytes, fibers or nanoparticles) to stabilize the resin nanoparticles against aggregation during drying. In that way, porous dry resin can be produced by air drying without complex experimental steps. Pyrolysis of the dry porous resins produces porous carbons which are suitable for applications in energy storage (supercapacitors), water purification (deionizers), energy conversion (fuel cells) or catalysis. Moreover, the size and distribution of pores can be controlled by the concentration of soluble stabilizers. On the other hand, hierarchical porous carbons can be produced by hard templating the resin with silica nanoparticles or cellulose fibers. The materials are characterized and properties relevant to technological applications are measured.

Chapter 15 - Oxygen reduction reaction (ORR) is one of the most interesting research issues in the academia and industries due to its importance in proton exchange membrane fuel cells (PEMFCs). Despite the advances in all kinds of catalysts, Pt-based materials are still the most efficient electrocatalysts for ORR. In particular, Pt-based nanomaterials with a porous or network-shaped structure possess intriguing physical and chemical properties to generate enormously promising potentials for ORR catalysis. This chapter attempts to summarize the recent advances in the design and synthesis of porous Pt-based nanostructured materials and their application as electrocatalysts for ORR in PEMFCs, including improved understanding of the reaction mechanisms and the development of synthetic strategies for producing catalysts with high activity and stability. Key scientific issues and prospective directions of research in this field are also discussed.



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*Chapter 1*

## **SYNTHESIS OF MESOPOROUS ALUMINA FOR CATALYTIC APPLICATIONS**

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### **ABSTRACT**

The synthesis of mesoporous alumina has a very interesting area of application, particularly as catalyst or catalyst support. This chapter focuses on the individual synthesis routes to produce mesoporous aluminas with large surface areas and narrow pore size distributions. The utilization of various structure-directing agents (cationic, anionic and neutral) during the preparation of aluminas was studied. The syntheses carried out with aqueous ionic surfactants produced aluminas with poorer textural properties than the aluminas prepared with nonionic methods in alcoholic solutions. It was found that textural properties of the aluminas differ depending on the preparation method. Some catalytic applications of mesoporous aluminas were cited. It was found that the stages of precipitation, aging and elimination of the surfactant, required more detailed experimental information.

### **1. INTRODUCTION**

The scientific advance in the design and preparation of heterogeneous catalysts has benefited from the studies of precipitated mesoporous materials using the cationic, anionic or nonionic procedures either silicon oxide ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ) or other oxides as titanium oxide ( $\text{TiO}_2$ ) and zirconium oxide ( $\text{ZrO}_2$ ) [1].

**Table 1. Template and synthesis conditions of the micro and mesoporous materials**

Example	Template	Synthesis conditions	Surface Area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)	Ref.
MCM-41	Ionic surfactant	basic	1128(550°C), 403(850°C)	0.95	ND	5
MCM-48	Ionic surfactant	basic	1433(550°C), 108(850°C)	1.14	ND	5
SBA-15	Ionic surfactant	acidic	632(550°C), 446(850°C)	0.63	ND	5
HMS	No ionic	basic	1021(550°C), 213(850°C)	0.81	ND	5
Alumina	Octylamine	basic	452(850°C)2. 52:14452:20: 21.6 12 51	0.81	5	10
Alumina	Dodecylamine	basic	418(450°C)	0.83	5	10
Alumina	Hexadecylamine	basic	434(450°C)	0.64	3.2	10
Alumina	C <sub>16</sub> H <sub>33</sub> NH <sub>2</sub>	basic	410(450°C)	0.60	3.0	10
Alumina	C <sub>16</sub> H <sub>33</sub> NH(C <sub>2</sub> H <sub>4</sub> NH) <sub>2</sub> HNH(4NH) <sub>2</sub>	basic	462(450°C)	0.63	3.1	10
Alumina	Me(CH <sub>2</sub> ) <sub>11</sub> OSO <sub>3</sub> Na	basic	ND (600°C)	ND	ND	13

ND = Non determined.

The design of supports have implications in the mesoporous phenomenon, in the internal mass transfer by diffusion of reactants and in the catalytic reaction, but especially in the controlled adsorption-desorption of reactants and products, for which it is important to control the pore size distribution [2-5], the surface area of materials and achieving high thermal stability (Table 1).

It has been known that alumina used as support or catalyst is most frequently applied in the chemical industry, and any improvements on their properties or in its manufacturing process is desirable [6].

The synthesis of alumina is more complex than the synthesis of mesoporous silicates, and these materials have been documented success in controlling the pore size and the formation of different types of active sites on their surface, For example, the synthesis of MCM-41 mesoporous silicates and aluminosilicates [7].

The successful synthesis of ordered mesoporous aluminas, reviewed by Marquez et al. [8], Cejka et al. [9], Pinnavaia, [10] and Li et al. [11], have resulted in some significant improvements in the textural properties of such mesoporous material, particularly as a catalyst.

The conventional aluminas have surfaces between 50-300 m<sup>2</sup>/g, and are prepared by precipitation [12]. These aluminas usually exhibit lower surfaces areas of less than 400 m<sup>2</sup>/g and the main disadvantage were their large pore size distribution, sometimes they show even more than one maximum in the range of 3-15 nm. For that reason, the successful synthesis of mesoporous alumina, with areas larger than 500 m<sup>2</sup>/g with a narrow pore size distribution is interesting [1].

These materials are characterized by having a high specific surface area and pore size distribution in the region of mesopores (2-10 nm) [13]. Some studies on the synthesis of

mesoporous aluminas using surfactants that have been cited where surfaces and pore size distribution were improved. However, these early forms of mesoporous aluminas were amorphous [14].

In accordance with Márquez et al. [8], the first successes in the synthesis of mesoporous alumina were reported by Vaudry et al. [15] using long chain carboxylic acids, and some attempts of the group of Stucky made lamellar systems only [16, 17].

In other procedure, the cationic route for preparing mesoporous alumina has been described by Cabrera et al. [18]. Using hexadecyl trimethyl ammonium bromide in combination with triethanolamine in water, the authors claim that by varying the ratio of surfactant, water and triethanolamine is possible to adjust the pore size between 3.3 and 6.0 nm.

Mesoporous alumina has been prepared by several routes: cationic, anionic, nonionic and the nanocasting methods, often they have surfaces between 300 to 700 m<sup>2</sup>/g and pore size of 2 to 10 nm or more. This type of alumina has application in several catalytic reactions, for example in the synthesis of hydrodesulfurization, epoxidation of styrene, partial oxidation of methane, oxidative dehydrogenation of ethane and metathesis catalysts [9]. The developing of mesoporous aluminas was preceded by the development of the mesoporous silicas

p-aminobenzoic acid

The first successful synthesis of mesoporous alumina was published several years later than the successful synthesis of silica and it is probably that this was due to the synthesis of mesoporous alumina is more complex compared to the synthesis of mesoporous silica [9].

This chapter aims to contribute to the update on the preparation of mesoporous aluminas using the cationic, anionic and nonionic methods. Some applications of this type of aluminas are mentioned.

## 2. GENERAL ASPECTS OF POROUS SOLIDS

Porous materials have shown significant physicochemical properties for use in separation processes and heterogeneous catalysis [19, 20]. Ideally a porous material should have a narrow pore diameter distribution which is important for the design of a catalyst. They should also show chemical stability, thermal or hydrothermal stability and mechanical strength, high area, large pore volume and have particle sizes and morphology appropriate.

Porous materials are defined in terms of pore diameter and adsorption properties. According to the IUPAC definition [21], porous solids are divided into three classes: microporous (<2 nm), mesoporous (2-50 nm) and macroporous (> 50 nm) [22].

Well-known examples of microporous solids are zeolites. These solids are crystalline aluminosilicates (natural or synthetic) with periodic three-dimensional structure, are microporous materials formed by regular arrays of pores and channels with uniform pore size [23, 24].

The porous oxides are crystalline solids, however, offer distinct advantages in regard to their use for various materials such as membranes, monoliths, and fibers. They can have a suitable molecular size to the process needs.



Mesoporous solids can be obtained, such as amorphous gels, aerogels and glasses. Unlike zeolites, these materials have a disordered pore system and therefore present a wide distribution of pore diameter. These materials are typically used in separation processes and as catalyst support [25-28].

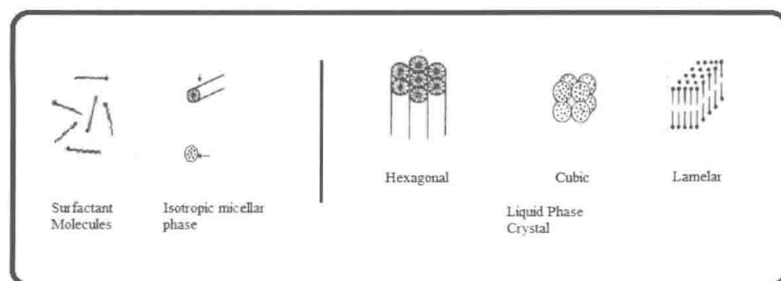


Figure 1. The role of the surfactant in aqueous solution to build the lamellar structure of mesoporous silica.

In the case of mesoporous solids based in silica (Figure 1), the role of surfactant in presence of water, the surfactant molecules are very active showing many structures in accordance with the increase of concentration. At low concentrations, the surfactant exists as mono-molecules and at high concentration is observed the formation of micelles. As the concentration increase, some arrangements named ensembles are organized in a close packing having a hexagonal shape (lamellar), but another geometric ensembles could be formed, for example cylinders which put in parallel arrangement produce a lamellar phase.

### 3. ALUMINA USING ANIONIC SURFACTANTS

Vaudry et al. [29] conducted a synthesis of mesoporous alumina by anionic route, stearic acid and lauric acids used as surfactants, alcohol and diethyl ether as solvent. The aluminum source used was an aluminum alkoxide. The obtained mesoporous alumina showed specific surface  $s$  in the range of 500-700  $\text{m}^2/\text{g}$ , with a pore size distribution around 2.0 nm (Table 2).

Sicard et al. [30] investigated the mechanism to remove the surfactant DSS from a mesoporous alumina using thermal analysis. The authors found that a strong interaction of the sulfate groups on the hydrophobic portion of the surfactant with the frame of the alumina during its formation was formed. This interaction probably caused sintering and collapse of alumina framework when the surfactant was removed. This explanation also has been reported by Valange [31].

In other studies Čejka et al. [32, 33] modified the procedure to synthesize the mesoporous alumina, using lauric acid and stearic acid as surfactants in a solution of 1-propanol. The samples prepared with lauric acid, calcined at 420°C showed a specific surface of 475  $\text{m}^2/\text{g}$ . The samples prepared with stearic acid showed specific surfaces of 700  $\text{m}^2/\text{g}$ . The pore diameter distribution showed a maximum of 3.5 nm. The same authors [32] showed that using stearic acid, the presence of micropores is not observed. These materials calcined at low temperatures do not exhibit crystalline structure by X-ray diffraction (XRD) and transmission electron microscopy (TEM) [33], however these aluminas were transformed into a crystalline phase when they were calcined at temperatures between 600°C and 1000°C.