Volume

2

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MATERIALS SCIENCE AND TECHNOLOGIES

Mahmood Aliofkhazraei
Editor

Comprehensive Guide for Mesoporous Materials

Application and Commercialization

NOVA

MATERIALS SCIENCE AND TECHNOLOGIES

COMPREHENSIVE GUIDE FOR MESOPOROUS MATERIALS

VOLUME 2

ANALYSIS AND FUNCTIONALIZATION

MAHMOOD ALIOFKHAZRAEI
EDITOR

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PREFACE

This is the second volume of the four volume set of the Comprehensive guide for Mesoporous Materials. Mesoporous materials are found abundant in biological systems and minerals and some of these materials have long been used in various industries. Recent advances at the nanoscale level has caused an increase in the use of these materials. This volume mainly discusses the analysis and functionalization of mesoporous materials.

Chapter 1 – The classification of pores with regard to their pore width is given. The standardisation and classification work concerning the surface texture of porous material is reviewed. A compilation is presented of methods which can be used to determine the total pore volume, the pore size distribution and the fractality. The survey comprises light, X-ray, electron, ion, acoustic and tunnel microscopy, mechanical sensing, classification of particle size, flow methods, volume and density measurements, intrusion, sucking and displacement porometry, gas or liquid sorption porometry, thermoporometry, desorption spectroscopy and nuclear magnetic resonance measurements. Furthermore, a method of saving time of sorption measurements is presented.

Chapter 2 – This chapter treats of the organization and functionalization of hybrid organic-inorganic mesoporous materials. These materials based on silica matrix were prepared by sol-gel process, which consists on the hydrolysis and polycondensation of silylated molecular precursors in the presence of a structure-directing agent. The authors described methods to functionalize the channel pores of ordered mesoporous silica, this of the silica framework as well as the functionalization of both of them simultaneously. Thanks to chemical modifications, they evidenced not only the accessibility but also the location and the regular distribution of the introduced organic units. This family is currently one of the best supports for exploring polyfunctional materials, which can provide a route to original nanomaterials.

Chapter 3 – A series of mesoporous titania materials modified with with tungstosilicic (TSA) were successfully synthesized using titanium isopropoxide as titania precursor and urea as low-cost template via sol-gel reactions. They were characterized by FT-IR, XRD, DTA-TGA, DRS, SEM and BET. The obtained mesoporous solids presented an average pore diameter higher than 3.1 nm. The specific surface area decreased when the TSA amount and the calcination temperature increased. The XRD patterns of the modified samples only exhibited the characteristic peaks of anatase phase. The presence of TSA retarded the crystallization of the anatase phase and its transformation into rutile phase. The FT-IR studies showed that the main heteropolyoxometallate species present in the composites is the

$[SiW_{12}O_{40}]^{4-}$ anion for the samples calcined up to 500 °C. The *band gap* energy slightly decreased as a result of the introduction of TSA into the titania matrix, though it remained almost constant with the calcination temperature increase. The 4-chlorophenol degradation behavior of the catalysts as a function of time depended on the TSA amount and the thermal treatment temperature. The amount of degraded 4-CP increased with the increment of TSA content being the sample containing 30 % TSA calcined at 600 °C the most active. The apparent reaction constant, estimated assuming a pseudo-first-order kinetics, followed the same trend. The catalysts can be reused at least three times without an important decrease in the degradation and mineralization degrees.

Chapter 4 – Pore walls in mesoporous silicates may exhibit dual, simultaneously crystalline and amorphous features. The extents of the two characteristics may be varied depending on the synthesis and further treatments. Their partitions can be followed with different methods. Examples are presented from studies performed on Fe-MCM-41 ferrisilicates synthesized with different procedures, by hydrothermal synthesis and by hydrolysis of tetraethylorthosilicate. Properties of samples are compared by applying primarily in situ Mössbauer and infrared spectroscopies complemented with XRD, BET, TEM, TPR methods. Flexibility in variations of the crystalline/amorphous parts is illustrated in dependence of the actual conditions. These structural changes can also be strongly correlated to $Fe^{3+} \Leftrightarrow Fe^{2+}$ redox processes.

Chapter 5 – The authors report the functionalization of mesoporous materials for improvement of the electrocatalytic properties. As silica and carbon based-materials are often used as template to synthesize other mesoporous, these materials are described here. The authors focus on ordered mesoporous carbons (OMC) because the functionalization and applications of mesoporous silicas have been well reviewed. They show how the ordered mesostructure of these materials is very important in the construction of (bio) sensors. Moreover, the structural capabilities of OMC at the scale of a few nanometers agree with immobilization of other electrocataytic substances. Interesting properties of these materials may open up a new approach to study the electrochemical determination of other biomolecules.

Chapter 6 – Nanoporous titanium dioxide was prepared by sol-gel technique. To control the surface area, pore size and pore volume of the prepared TiO_2, a catalyzed hydrolysis was carried out using different concentrations of silicotungstic acid (SWA) as a template. A fixed molar ratio of H_2O/Ti was used. The prepared TiO_2 was calcined at 400 or 600°C. Samples were characterized by nitrogen physisorption, X-ray powder diffraction (XRD), selected scattered electron diffraction, Raman spectroscopic analysis, Fourier Transform spectroscopy (FTIR), Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), scanning and transmission electron microscopy (SEM and TEM). The photocatalytic activity of the prepared samples was evaluated by the degradation of alizarin yellow under UV light. The results showed that the crystallinity increases as the concentration of SWA decreases. The presence of SWA during the precipitation of TiO_2 prevents the formation of rutile phase and suppresses the crystal growth. The results showed also that the surface area increase as the concentration of SWA decreases. The samples prepared using 0.05M SWA and calcined at 600 °C showed a higher activity.

Chapter 7 – In the early nineties, quickly after the discovery of ordered mesoporous solids, some strategies for organic functionalization were developed. Concerning the organic functionalization of ordered mesoporous silicas, the conventional post-synthesis grafting from

organosilane reagents on surface silanols and the direct synthesis via co-condensation of alkoxysilane and organosilane precursors have been widely studied, compared and reviewed. The recent societal tendencies such as evolution of researches in the field of materials towards the concept of eco-conception and biologically oriented applications have provoked the emergence of new organic functionalization strategies in terms of processes, reactants and controlled functionalization. The characterization of these organically-modified ordered mesoporous solids is of paramount importance for understanding the structure-properties relationships in order to produce tailor-made hybrid mesoporous materials. Some progresses have also been done in this area and especially with the powerful and well-adapted technique for the characterization of such solids consisting in solid state NMR spectroscopy. These evolutions in both organic functionalization strategies and functionalization characterization by NMR are highlighted in this book chapter.

Chapter 8 – The application of nanoscale materials and structures is an emerging area of nanoscience and nanotechnology, with broad scientific and commercial perspectives. The high surface energy of the inorganic materials, such as metal and metal oxides, mainly determined by size, shape, composition, crystallinity and morphology has attracted lots of attention in functional nano-finishing of textiles. The purpose of this work is to highlight the added-value technologies based on nanoparticles contribution, focusing on functional textiles with higher quality attributes, such as: antimicrobial properties, water repellence, electro-magnetic protection and thermoregulatory fabrics, antistatic, anti-infrared and flame retardant properties, dyeability, colour fastness, as well as durable, or permanent press finished garments, textiles with self-cleaning properties, UV-blocking, deodorizing, thermal regulator, memorizing shape, and so on. The use of the nanoscale materials in the textile manufacturing opens many opportunities towards the production of so-called "intelligent textiles".

Chapter 9 – The authors report on the structural and optical properties of mesoporous silicon nanowires (PSiNWs) fabricated using silver ions assisted electroless etching method. The strongest photoluminescence signal has been measured from samples etched with 4.8M of HF. Reflectance were measured versus nanowire length and were inferior to 0.1%. Models based on cone shape of nanowires located in circular and rectangular bases were used to calculate the reflectance using the Transfert Matrix Formalism of *P*SiNWs layer. The modeling of the reflectance permits to explain this value by taking account into the shape of the nanowires and its porosity. Optical absorbance and transmission were also theoretically studied. The absorbance was superior to that obtained with silicon nanowires and the ultimate efficiency was about equal to 25% for normal incidence angle. These results could be applied to the potential application in low-cost and high efficiency *P*SiNWs based solar cells.

Chapter 10 – Mesoporous TiO_2 thin films had been prepared through sol-gel combined with evaporation-induced self-assembly (EISA) by using F127 and $Ti(OBu^n)_4$ as templating agent and inorganic precursor respectively. It was found that the calcinations temperature, relative humility and the mass ratio of templating agent to inorganic precursor could vary the TiO_2 mesoporous structure. The thermodynamic study for the sample had been carried out and the critical crystallite size expression of the mesoporous film based on the authors' established four-coordinate channel model was presented for the prediction of the thermal stability of the mesoporous structure at high temperature. Varying the amount of templating agent to inorganic precursor could adjust the pore size and structure of mesoporous TiO_2. When the mass ratio of F127/$Ti(OBu^n)_4$ varied from 0.1 to 0.5, the pore sizes of mesoporous TiO_2 changed from 5.4nm to 9.1nm. The pore size regulation mechanism had been discussed.

N, S co-doped TiO_2 exhibited framework with a high porosity. Both pure mesoporous TiO_2 and N,S co-doped TiO_2 exhibited higher photocatalytic activity, especially for the N,S co-doped samples.

Chapter 11 – This chapter deals with the Inversion or Inflection point(s), termed collectively *I-point(s),* which appeared in all the N_2 adsorption isotherms $V=f(P/P_o)$ of porous solids. The *I-point(s)* correspond to the equivalent point(s) of titration of the adsorbent material (analyte or titrand) by the adsorbate N_2 (titrant or titrator) at 77K. If there is just one I-point, this corresponds to the completement of physical adsorption and is useful for the determination of the specific surface area -*ssa*- of solid (S_p, m^2g^{-1}) without any knowledge or use of the traditional BET methodology. If there is a second equivalent point, this corresponds to the completement of the condensation of N_2 into the capillary pores. The *I-point(s) method* is a precise and convenient procedure for estimating the *ssa* of porous materials based on N_2 adsorption data, $V=f(P/P_o)$. Such data if plotted in the form $V(1-P/P_o)/(P/P_o) = f(V(1-P/P_o))$ may show one I-point, if mesopores are spatially mixed with micropores (case i) or two I-points if the mesopores form separate domains in the porous solid (case ii). The projection of the single I-point (case i), or the low pressure I-point (case ii), on the $(V(1-P/P_o))$ axis corresponds precisely to the volume of monolayer V_m from which the S_p values can be easily estimated ($S_p = 4.356V_m$ for N_2). Finally the variable slope of the I-plots corresponds to the *variable equilibrium constant C of adsorption,* introduced in the BET equation, which is not attainable via the classical linear treatment.

Chapter 12 – In most cases the chemisorption process is described in terms of formation of adsorbate complexes of 1 : 1 stoichiometry, *i.e.* one surface site binds one adsorbate molecule. However, there are two more possibilities: (i) one adsorbate molecule bridges more than one site and (ii) one site binds two or more adsorbate molecules. The second possibility is typical of cations in porous materials. In this chapter the authors summarize the achievements on why and when two or more identical or different molecules can be simultaneously attached to one cationic site.

Chapter 13 – Crystalline layered silicates, which possess two-dimensional nano-spaces between the layers, have been utilized for various applications, as adsorbents, catalysts/catalyst supports, ion exchangers etc. These uses are possible due to the covalent modifications on the silicate surface SiOH/SiO^- groups. This chapter will examine the feasibility of synthesizing organo–inorganic composites based on layered silicates. It aims to explore the basic and advanced aspects of preparation and characterization of silylated and/or pillared interlayered clays by quaternary ammonium salts pre-swelling step, which is responsible for the controllable and designed pore structure and accessibility.

Chapter 14 – Ordered mesoporous and non-porous silica films were studied by analyzing angular and spectral dependencies of reflectivity and hemispherical elastic light scattering (HELS). The real and imaginary parts of the film index were estimated from the reflection spectra. The HELS angular distribution of the mesoporous film shows a minimum, which has been interpreted as an interference pattern coming from light scattered by continuous set of the mesopores. Another mesoporous Al_2O_2 membrane (a 2D periodic array of empty and metal-filled linear nanopores) has been studied. These mesoporous membranes are characterized by noticeable differences in reflectance. A Maxwell-Garnett's (MG) model of composite material has been used to recover the dielectric function of tin nanorods. A consistent explanation of the optical properties has been achieved using multiple scattering and metallic behaviors of the nanorods.

Chapter 15 – The interest of worldwide scientists on developing functional materials with special properties that allow their use in emerging fields as biomedicine and environmental remediation has continuously grown in the last several years. Due to their structure and surface properties mesoporous molecular sieves offer possibilities to be modified in a controlled manner to obtain important materials with specific applications in emerging fields. Silica- and carbon-based mesoporous molecular sieves modified with iron oxides (magnetite and hematite), titanium oxide (anatase), bismuth oxide (alpha-Bi_2O_3) by controlled encapsulation were developed. Their functionalities and specific applications in biomedicine and environmental remediation are discussed in separate sections.

Chapter 16 – The synthesis and characterization of Pd-poly(N-vinyl-2-pyrrolidone)/CMK-8 (Pd-PVP/CMK-8) composite and its application in Suzuki-Miyaura cross-coupling reaction as a novel heterogeneous catalyst is reported. The catalyst was characterized by FT-IR, XRD, XPS, BET, TGA, DRS UV-Vis, SEM and TEM techniques. The catalytic activity of this purely organic hybrid catalyst was compared with Pd-PVP/KIT-6 to clarify the advantages of mesoporous carbon on mesoporous silica as support. Surprisingly, the composite prepared by mesoporous carbon showed much higher activity than that of Pd-PVP/KIT-6. In addition, the results showed that the stability of Pd-PVP/CMK-8 was excellent and that it could be reused 13 times without much loss of activity in Suzuki reaction. This unique result opens new perspectives for application of mesoporous carbons as structurally defined hydrophobic catalyst support in catalytic reactions.

CONTENTS

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Chapter 1

MESOPOROUS SURFACE STRUCTURE ANALYSIS

***Erich Robens*[*1] and Shanath Amarasiri A. Jayaweera*[#2]**
[1]Uniwersytet Maria Curie-Skłodowska, Lublin, Poland,
[2]Stokesley, Middlesbrough, UK

ABSTRACT

The classification of pores with regard to their pore width is given. The standardisation and classification work concerning the surface texture of porous material is reviewed. A compilation is presented of methods which can be used to determine the total pore volume, the pore size distribution and the fractality. The survey comprises light, X-ray, electron, ion, acoustic and tunnel microscopy, mechanical sensing, classification of particle size, flow methods, volume and density measurements, intrusion, sucking and displacement porometry, gas or liquid sorption porometry, thermoporometry, desorption spectroscopy and nuclear magnetic resonance measurements. Furthermore, a method of saving time of sorption measurements is presented.

1. INTRODUCTION

Most solid material contains pores, in the bulk and/or on its surface. The large porous structure of a solid is important in its applications and for reaction with the environment [1-6]. Applications include storing of gases and liquids, chemical reactions with a solid surface and heterogeneous catalysis. Thus characterisation of a solid material always includes the investigation of its pore structure. The following survey brings to focus the investigation and characterisation of mesoporous structures providing a large surface area.

The majority of porous materials have pores within a wide range of size. On the other hand investigation methods are restricted into their measuring range. Therefore we can hardly

* Schlesierstr. 5, D-61381 Friedrichsdorf, Germany, hon. prof. Uniwersytet Maria Curie-Skłodowska, Lublin, Poland, *formerly*: Battelle-Institut e.V., Frankfurt am Main, Germany. erich.robens@t-online.

42 Tanton road, Stokesley, Middlesbrough TS9 5HR, UK. *formerly* Teesside University, School of Science & Engineering, Middlesbrough, United Kingdom. saajayaweera@yahoo.co.uk

define a 'true' characteristic pore. It is better to determine size distributions rather than characterising values. In each case we should indicate the measuring method used and its limits. Problems arise when measuring conditions deviate markedly from application. It is advisable to apply several different measuring methods in parallel allowing for critical validation of the results. At the end the measurements should be supplemented by practical experiments.

Measuring methods need to be validated. Validation is the process of determining the suitability of methods for providing useful analytical data with the required accuracy [7-8]. Guidelines for validation procedures are elaborated and standardized at international level [9-10]. All measurements are burdened with errors and uncertainties which should be indicated [8].

2. DEFINITIONS

Pores mostly are of irregular shape; Figure 1 shows schematically a porous grain with different types of pores.

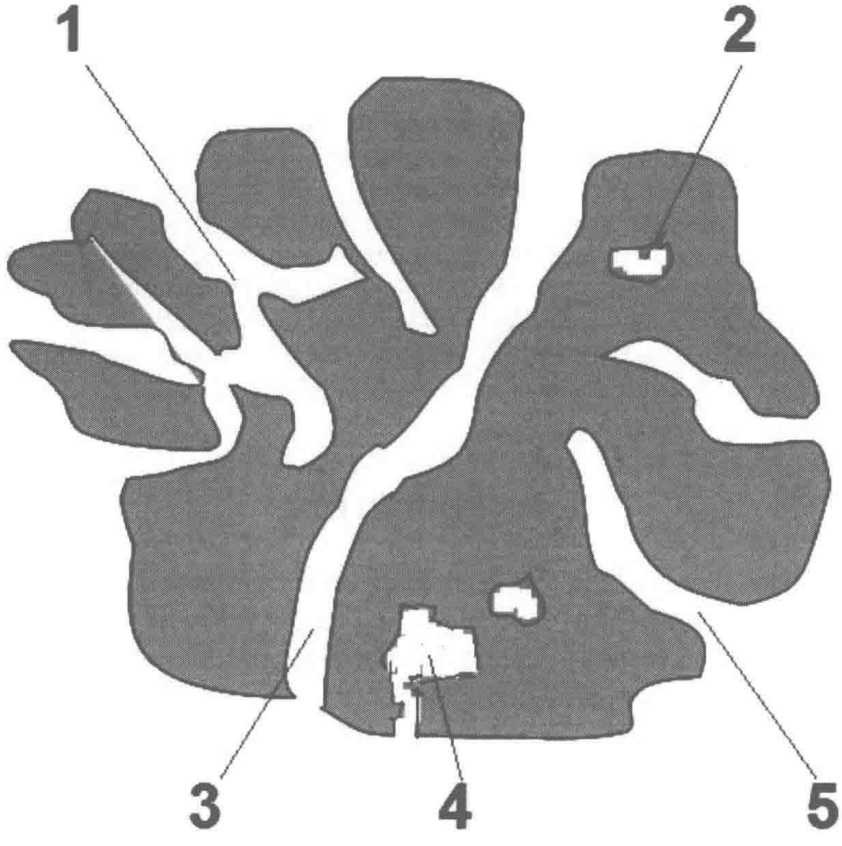

Figure 1. Diagram of a particle with different pore types: 1 inter-connecting, 2 closed, 3 passing, 4 ink bottle, 5 dead end.

Following definitions concern pore models of simple geometry. It is customary to express the average width d of a cylindrical pore as:

$$d_P = \frac{4\,V_P}{S_{smooth}} \tag{1}$$

The volume of a cylindrical pore or particle is given by:

$$V_P = \pi\, r_P^2\, h = \frac{\pi\, d_P^2\, h}{4} \tag{2}$$

The volume of spherical pore or particles is given by:

$$V_{sph} = \frac{4\,\pi\, r^3}{3} = \frac{4\,\pi\, d^3}{24} \tag{3}$$

Pores are classified by several authors: Dubinin [11], IUPAC [12], Setzer [13] (Figure 2):

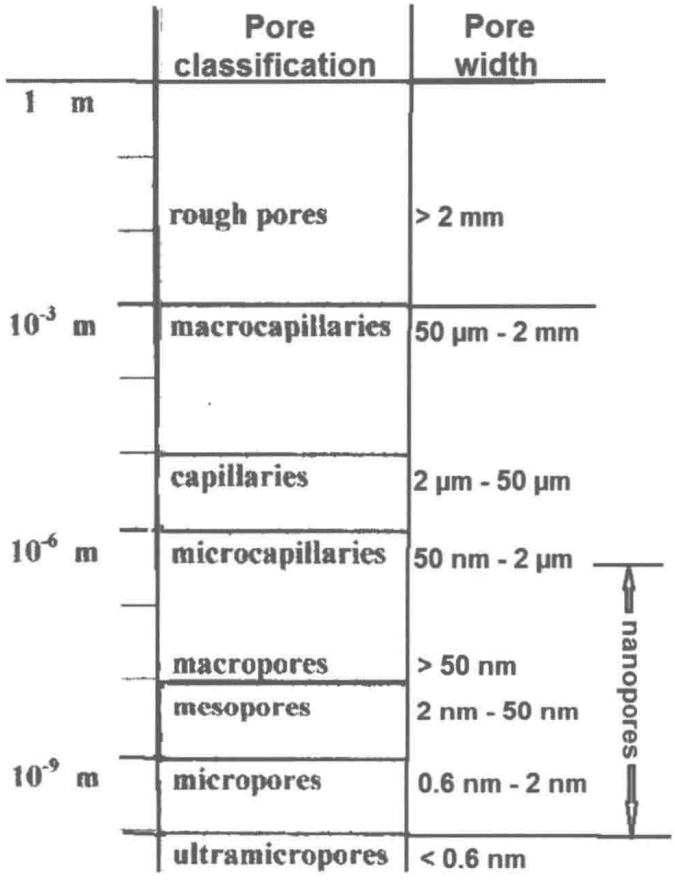

Figure 2. Pore classification according to Setzer (capillaries), IUPAC (pores), and Dubinin (ultramicropores).

3. MEASURING METHODS

In Table 1 methods, which are used to investigate surface and internal structure of solids are presented. In Figure 3 the detection limits of the different methods are depicted. In principle the porous structure can be directly investigated or the matrix is filled with a fluid and that fluid is investigated.

Table 1. Methods characterising the surface and pore structure

Method	Instrument
Mechanical tracing	Surface roughness tester, mechanical profiler Scanning tunnel microscope (STM) Atomic force microscope (AFM)
Classification, Sedimentation	Classification (sieving, air separation)
Flow methods	Andreasen pipette Blaine apparatus Liquid flow
Optical methods	Optical profiler Microscope Electron microscope Ellipsometer Holography Small angle X-ray scattering (SAXS) Powder diffractometer
Density determination	Gas pyknometer Buoyancy in a gas, Millikan / Straubel apparatus Hydrostatic balance,
Intrusion porometry	Mercury porosimeter Water porosimeter
Gas adsorption	Gravimetric sorption apparatus Volumetric sorption apparatus Gas flow apparatus
Adsorption from solution	Quartz oscillation microbalance
Size exclusion	HPLC apparatus
Calorimetric methods	Calorimeter
Thermoporometry	Calorimeter

Tracing

By mechanical tracing a surface with a needle, we obtain the roughness factor as the relationship of the recorded length to its linear projection. From the roughness measured in two perpendicular directions we can calculate the surface area. Conversely we can calculate the roughness factor from a surface area determined e.g. by gas adsorption. The resolution limit of the tracer method is given by the tip radius. Because that pin should resist wear, only diamond can be used. A tip radius of about one micrometer can be realized.