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THE ORIGIN OF NANOPORES*

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The survey covers the methods of producing pores of nanometer width. Features of such nanomaterials differ remarkably from both that of nanoparticles and that of materials with pores in the micrometer range.

Keywords: *adsorption, mesopore, micropore, molecular sieve, nanopore*

Introduction

Production and application of particles with diameters of up to some ten nanometers is a recent technique [1, 2]. In contrast materials containing pores of such width had been applied as adsorbents already in antiquity [3–7]. The industrial production of activated carbon started in 1900 and of zeolites in the 1950s. In imitation of the denotation nanoparticles recently this group of pores is called nanopores [8–10]. With regard to sorption and condensation effects the IUPAC introduced a classification of pores [11]: pores of internal width greater than 50 nm are classified as macropores, less than 2 nm as micropores, and between as mesopores. Indeed, the term ‘macro’ for >50 nm is awkward and the term ‘micro’ is misleading because the width of micropores is between 0.6 and 2 nm! This classification was extended by Setzer [12, 13] for the macropore range with regard to penetration and condensation effects in building materials and by Dubinin [14] for the micropore range in order to discuss pore filling phenomena at low relative pressure.

Nanoparticles consist of only few molecules. They expose a large specific surface area to the adjoining fluid phase. Its physical and chemical properties can deviate remarkably from large compacts. Nanoparticles can pass through certain membranes; e.g. nano-sized drug particles can penetrate the skin and other biological barriers. In contrast nanopores preclude the infiltration of large molecules: adsorption is selective. Diffusion of fluid molecules is obstructed by tortuous channels and bottlenecks. On the other hand molecules from the adjoining fluid phase are adsorbed at the inner surface at the pore walls which mostly is much larger than the outer surface and condensation takes place within the pore volume. Effects in nanopores ≡ meso- and micropores differ remarkably from those occurring in macropores. In so far we may notice a similarity to nanoparticles.

Pore means an indentation which is deeper than wide [15]. Using this definition, most surfaces can be regarded as porous. Even when the primary particles of a powder are non-porous, an aggregate or an agglomerate of particles is expected to develop a porous body. Taking into account the variety of processes generating a pore structure, like chemical attack, thermal degradation of constituents, exfoliation, swelling, evaporation of crystal water or other volatile species, dissolving away of components, lattice alteration, we should realise that the vast majority of solids in our surrounding is porous. There are in principle three ways to produce a porous material: aggregation of particles, subtraction of a component from a compact body and structural changes (crystallisation). Basic processes applied in techniques or occurring in nature include only few methods as listed in Table 1. Applying those methods we may obtain pores of any width in dependence of process parameters chosen.

The present paper should be regarded as an essay on a methodical survey of processes which result in a porous structure with emphasis to nanopores. Based on Mikhail’s [16] suggestions we extend earlier considerations on general principles of formation of porous solids [17].

Compaction of powders and sintering

The simplest way to produce a porous system is compaction of particles [18]. If the original particles are

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non-porous the pore space is made up of the interstitial voids. The pore volume will depend on the particle size and – in the case of uniform particles – on the average coordination number. In the general case of a heterogeneous mixture of particles of various size and shape the porous structure and volume depends strongly on the pressure exerted.

With increase in temperature, sintering commence. For metal powders, three stages of sintering can be distinguished [19]:

- Smoothing of the surface of the discrete particles by surface diffusion, elimination of nanopores. Some loss of both, specific surface area and pore volume is observed.
- Adhesion. Discrete particles, which at low temperature constitute a loose powder, develop points of contact. The powder is converted into an aggregate that has little mechanical strength. This stage occurs near the Tammann temperature, which is approximately half the absolute melting point. There is some surface transport, and bridging between particles by curved-neck connection begins. The solid mass contains macro- and mesopores; a little decrease of specific surface area is observed. If the surface transport is extensive, closed-off pores may develope, which are not connected to the outside.
- Shrinkage. Further heat causes onset of shrinking with fastening of bridges between particles. Crystal grain growth takes place. More pores lose their connection to the exterior. The entire porous body shrinks. In the final stage of this process, the isolated voids are eliminated by diffusion of vacancies, which readily occurs at grain boundaries.

This classical mechanism of sintering does not hold for very fine particles of diameter 100 nm and less. For example, in the case of fine TiO_2 particles, the contact between two adjacent particles does not form a curved neck [20]. Initially spheroidal particles become polyhedral and adhesion then occurs between the flat surfaces.

Compaction pressure leads in most cases to a decrease in pore volume and surface area whereby in case of a broad particle size spectrum the reduction is more pronounced. This decrease is attributed to the fact that fine particles are flaky, with an extensive area of very flat surfaces, which is eliminated when they are forced to adhere to each other. The effect of pressure depends strongly on the mechanical properties of the solid. For example, plastic deformation governs the response of sodium chloride, whereas particle fracture governs the compaction of both, sucrose and coal [21]. With sucrose, the fragments move to occupy the available space, while with coal there is a tendency to form bridges and to preserve the open pore structure. After such a change in the pore structure the temperature required for sintering is often higher.

Gel precipitation

In a certain state of fine division, particles with diameter below about 200 nm are called colloids. Mixed with a fluid colloids form a colloid solution: the sol. By spontaneous coagulation or supported by some changes of the solvent properties (pH value, temperature) or by concentration the particles adhere to each other and take on the form of a gel. Extraction of the solvent produces an aerogel whereas evaporation leads to a xerogel.

Metal hydroxide or hydrous oxide gels and precipitates can be obtained from solution in a wide range of pore structures. The process includes a sol–gel reaction, hydrolysis and polycondensation. An organic template may be added by which the pore width can be influenced. This template is decomposed during the drying process. After precipitation of the sol in some cases leaching and/or solvent exchange is performed. Once the gel is formed it starts ageing. It undergoes structural and textural changes, which continue during after the removal of the liquid. Three stages have been described [22]:

- Condensation, polymerization, often accompanied by the development of a large surface area and the creation of uniform nanoporosity.
- Aggregation, cementation. This involves loss of area with concomitant loss of nanopores and development of pores micrometer width.
- Crystal growth and recrystallisation is a slow process unless accelerated by heat. It leads to the elimination of pores and the ultimate production of stable, crystalline solids of low or negligible porosity.

Elimination of the liquid phase generally leads to a slowing down in the rate by which that three processes take place. In certain cases another pore structure is generated. An example is the aerogel structure with large pore volume. Such a structure collapses upon heating, with a tremendous reduction in pore volume, but only a small change in specific surface area. This occurs to a lesser extent in the conversion of a hydrogel to a xerogel, which involves only a partial collapse of the structure.

Precipitation of insoluble compounds other than hydroxides can lead to gels; but the following steps are commonly much simpler than those with metal hydroxides. Principally a crystal growth occurs, with disappearance of the smaller and more imperfect crystals. Porous solids prepared from such precipitates commonly have pore morphologies resembling to those obtained with compacted powder.

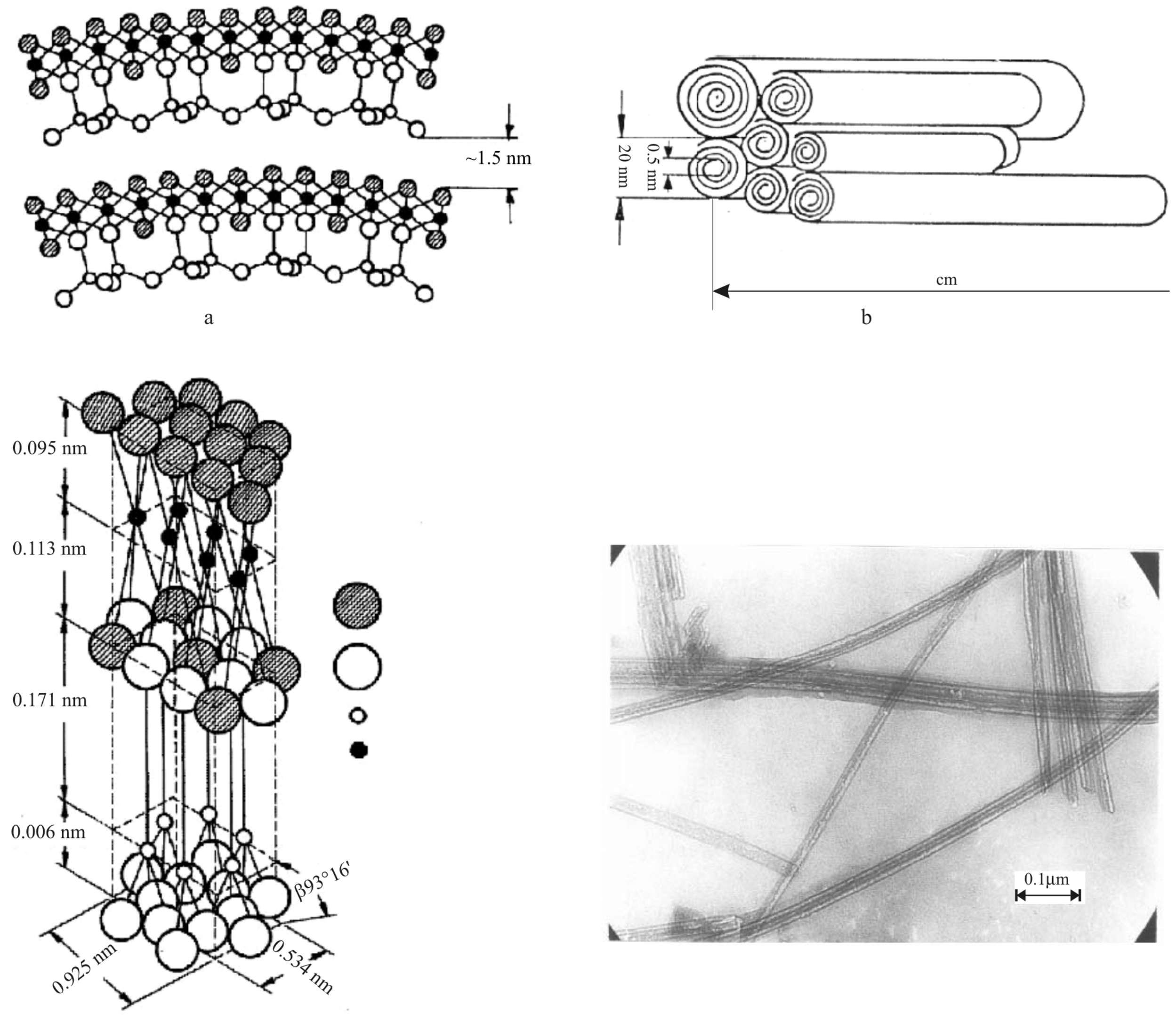

Fig. 1 Chrysotile asbestos: a – bent parallel layers of fibrils, b – crystal structure, c – fibrils parallel packed to fibres, d – transmission micrograph of single asbestos fibrils [24]

In some cases, a primary solid is capable of further chemical reactions with water leading to a gel which is precipitated in the water-filled spaces of the primary structure. It can undergo a subsequent change of composition, and shrinkage, leading to a microporous structure. Typical examples are Portland and other cements, as well as gypsum.

When dry cement is mixed with a limited volume of water, it forms a cement paste. It exists initially as a conglomerate of discrete particles of the unhydrated cement grains and calcium sulphate [23]. In the presence of water, this develops into a conglomerate of ‘cement gel’, calcium hydroxide, small amounts of other coarsely crystalline hydration products and residual unhydrated cement grains. The remnants of water-filled space that had existed at the start of the process give the matrix for meso- and macropores (capillaries). Micro- and mesopores are widened by penetration of additional water layers. During this swelling process stable pore structures are not observed [24]. The hardened gel itself consists of finely divided colloidal hydration products, which are mostly calcium silicate, and 'gel pores' between, filled with water. The water can be removed reversibly by evaporation as can be the water in the capillary pores. The pore width is between 1.5 and 3 nm.

In contrast to the characteristic volume and size of the gel pores, the capillary pore volume can vary, depending on the water/cement ratio, and the degree of hydration. The capillary pores constitute an interconnected network in the fresh cement paste. The pores become discontinuous as hydration proceeds. When this occurs, transmission of fluid between capillary pores must involve passing through gel pores, whose size is very much smaller.

Crystallisation

Clathrates are so-called inclusion compounds. Its lattices contain isolated cavities which are stable only when filled with guest molecules [25].

Chrysotile asbestos is an interesting porous mineral [26] with very regular pores ranging from ultramicropores to macropores. With regard to health hazards the material is in general out of application. Probably because of the geometric shape of the fibrils (small and sharp needles which are somewhat longer than a macrophage), when breathed in from the air, can cause not only asbestosis, but can also generate mesotheliuma. Chemically it is pure magnesium silicate (Fig. 1a) the molecules forming spiral layers wound up to small fibrils of about 20 nm in diameter (Figs 1b, c, d). The fibrils are densely packed to fibres of diameters in the micrometer range. The gaps between the spiral layers form ultra-micropores which are not accessible for any foreign molecules.

Zeolites and molecular sieves are examples of a group of solids, in which an intercrystalline micropore structure is distributed as channels, slits, or cavities within the lattice [27, 28]. The dimensions and patterns of these micropores are regular. In addition a permanent dipole, the possible polarisation by an induced dipole and van der Waals interaction result in a high selectivity. Thus, the schematic depiction as geometric bodies (Fig. 2) misleads because only the geometric molecular sieving aspect is insinuated.

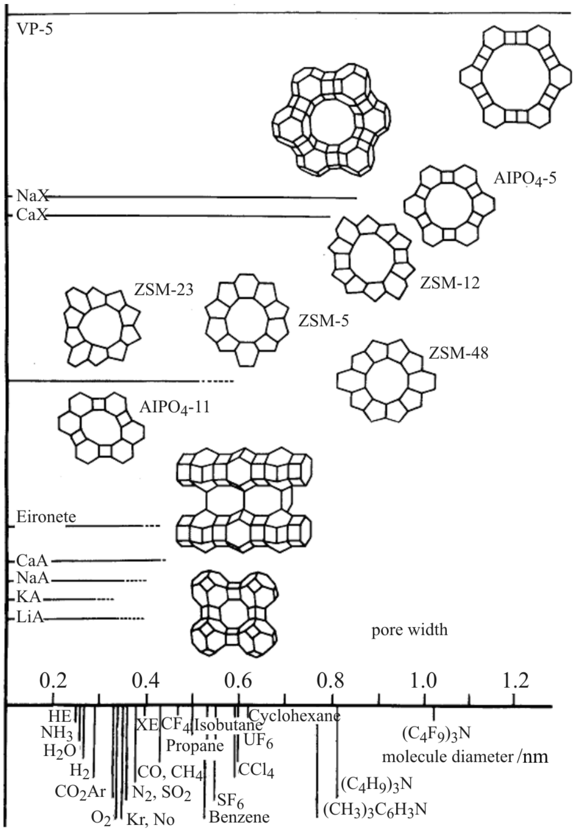

Fig. 2 Comparison of the pore width of molecular sieves and diameters of sorptive molecules according to Müller [31]

34 natural zeolites are known and about 150 types have been synthesised. The basic formula for zeolitic molecular sieves is $Mg_{2/n}O{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}yH_2O$ where Mg is a cation of *n* valence [29]. The fundamental building block of the molecular sieve crystal is a tetrahedral with four oxygen anions surrounding a smaller silicon or aluminium cation. Sodium ions or other cations make the positive charge deficit in the alumina tetrahedra, and each of the four oxygen anions is shared, in turn, with other silica or alumina tetrahedron to extend the crystal lattice in three dimensions [30]. In all molecular sieve types, the sodium ion can be exchanged to form other functional products. The crystal structure of zeolite molecular sieves is honeycombed with relatively large cavities containing water. The cavities are interconnected by 'windows' of diameter 0.3 to 1.2 nm. Before use the hydration water is removed by heating.

Natural zeolites are impure and erratic and therefore useless for industrial application. On economic reasons only the artificial zeolites types A, X, Y and MFI are used in industrial adsorption: it should be mentioned that industrial products of zeolites mostly are offered as pellets which are formed by addition of binding agents like clay which dispose of an additional pore system. There exist several types (Fig. 2):

- Type A has the formula $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]{\cdot}27H_2O$ whereby Na^+ can be replaced by other cations. Type A contains roughly spherical cavities ~1.1 nm in diameter and ~0.925 nm^3 in volume.
- Type 3A crystals are produced when some of the sodium ions are replaced by potassium ions. Since potassium ions are larger than sodium ions, the pore size is effectively reduced to about 0.32 nm.
- Type 4A sodium-bearing crystals have a free aperture size of 0.35 nm in diameter. At typical operating temperatures, molecules with effective diameter of up to 0.4 nm may passed through.
- Type 5A is produced by replacing some of the sodium ions in 4A with calcium ions. It features the largest pore opening of the A types, with a free aperture of 0.42 nm in diameter.
- Type X has the formula $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]{\cdot}264H_2O$, whereby Na^+ can be replaced by other cations. Although type X is based on the same building blocks as type A, the beta cages are linked tetrahedrally instead of a cubic arrangement.
- High silica molecular sieves have a significantly higher proportion of SiO_2 to AlO_2 in their molecular structure. With the reduced amount of AlO_2 and the corresponding reduction in cation density, the high-silica zeolites are hydrophobic and organophilic adsorbents.

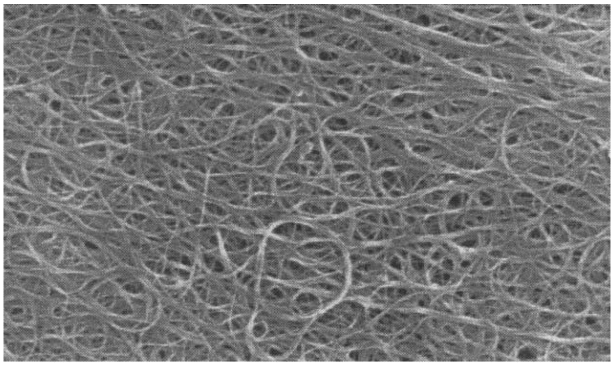

Fig. 3 Carbon nanotubes. Nanotube Incorporate, Houston, Texas [32]

Industrial production of zeolites comprises the mixture of batch-weighed quantities of sodium silicate, alumina trihydrat and sodium hydroxide. After stirring the mixture forms a gel that is pumped into a crystallisation tank. A rotary filter separates and washes the zeolite crystal slurry. For cationic exchange (calcium, potassium or other cations substituted for sodium in the crystal), the filter cake is transferred to a heated tank and mixed with the appropriate metal salt solution, and washed and filtered again.

Chemical treatment of solids

Many precipitation processes result in amorphous powders with small sized and often porous particles. Small pores down to nanometer width can be produced by treating the non-porous solid with a reagent which dissolves out some constituents, leaving a porous framework. In the preparation of porous Vycor glass a discrete phase that has been precipitated in advance during thermal treatment of the parent glass is dissolved by acid treatment [31, 32]. A three-dimensional porous network is generated resembling interconnected wormholes. Also Fuller's earth is produced by acid treatment of the mineral. The pore structure of the leached material depends on several variables: time and rate constant of the reaction, together with kinetic factors such as concentration and temperature, and the physical structure of the parent solid.

There are cases, in which a liquid reacts with a constituent of the parent solid, with collapse of the primary lattice. In the production of Raney nickel [33] together with leaching material transport by local electrochemical cells, anodic oxidation and cathodic reduction occurs.

A variety of processes are described to produce porous nanomaterials. In a CO atmosphere at 1000°C from a CO–Fe compound the iron atoms are separated and form little clusters and CO reacts: $2CO=CO_2+C$. By catalytic action of the iron clusters from C carbon nanotubes are produced with monomolecular walls (Fig. 3). In this way larger amounts of nanotubes may be produced which are extremely hard. Its electrical conductivity [34] depends on the molecular carbon structure and varies between that of a metal and of a semiconductor. Also catalytic peculiarities are to be expected.

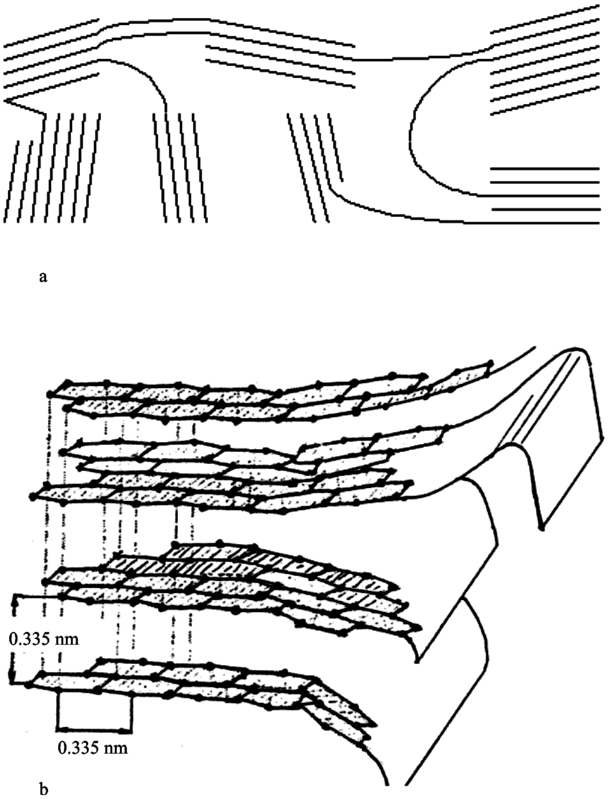

Fig. 4 Activated carbon. a – structure of activated carbon, b – graphite grid in layers of activated carbon

Thermal treatment of solids

When a non-porous solid material calcines to yield a solid product and a gas mostly pores are developed with tremendous increase in surface area [35]. Examples are the calcination of hydroxides, carbonates, and oxalates. Upon decomposition of a parent crystal a number of crystallites may generated in a metastable condition or a pseudo-lattice. They tend to recrystallise and sinter if heated. The overlap of the two processes activation (decomposition) and sintering/recrystallisation, leads to a maximum in surface area *vs.* calcination temperature. The presence of water is often found to accelerate the second stage of sintering.

Pyrolysis is a common process, used for the production of active carbon by the carbonisation of organic materials [36]. In the absence of air a low surface area is developed. It can be activated by steam or carbon dioxide. In the latter case oxidation and burn-

Table 1 Methods of preparing porous material

Basic methods of preparing porous material
Aggregation of particles
Subtraction of a component from a compact body
Structural changes like crystallisation
Inflation of a structure for example by swelling
Special methods of preparing porous material
Compaction of powder
Chemical reaction and precipitation
Sol–gel processing
Crystallisation
Thermal treatment

out of some components takes place simultaneously, with both a great increase in area and the production of active adsorption sites. Chemical additives or agents which catalyse these processes have been suggested for carbonising material of vegetable origin. Depending on the nature of the parent material and by adjustment of the reaction conditions and temperature pore sizes covering the micro-, meso- and macropore range can be obtained (Figs 4 and 5).

Pyrolysis may be applied to any cross-linked polymer. Even while gaseous products are evolved the material may retain much of his original configuration during heating. Low-molecular substances, for example coal, polymerise when heated, before they evaporate, and form viscous liquids before decomposition is complete. Gas that is evolved is held as bubbles, and surface tension will cause the pores that are produced to be roughly spherical in shape. As a final step, cross-linking occurs by which the pore structure is fixed. The pores tend to be of large size and of low area and are often closed.

Polymeric adsorbents

Raw materials for polymeric adsorbents are polystyrene, polyacrylate and phenol-formaldehyde. Polystyrene and polyacrylate adsorbents are produced by polymerisation whereas adsorbents based on phenol–formaldehyde by condensation [37]. Polymeric adsorbents are highly porous structures whose internal surfaces can adsorb a wide variety of different species depending on the environment in which they are used. For example, in polar solvents such as water, polymeric adsorbents exhibit non-polar or hydrophobic behaviour and so can adsorb organic species that are sparingly soluble. The hydrophobicity is most pronounced with the styrenic adsorbents. In non-polar solvents, such as hydrocarbons, most adsorbents exhibit slightly polar or hydrophobic properties and so will adsorb species with some degree of polarity. This polarity is most pronounced with the acrylic and the phenolic adsorbents. As already mentioned in the context of molecular sieves the geometric characterisation of the porous structure of polymeric adsorbents is questionable.

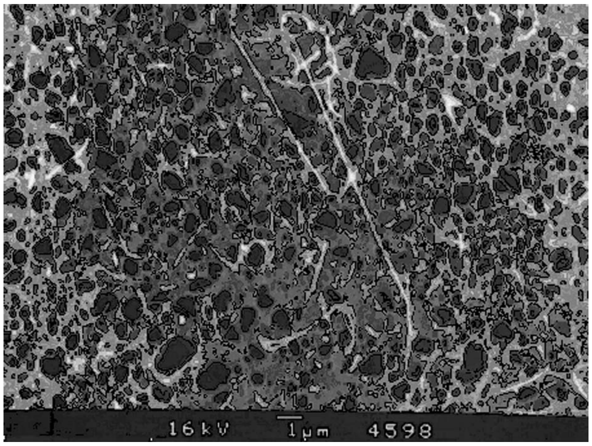

Fig. 5 SEM micrographs of the 'amorphous carbon-catalyst particles' surface after graphitization at 800°C in nitrogen flow: graphite nanotubes grow from the surface and then intergrow inside one [34]

A new class of adsorbents was developed by sulfonating porous resins and producing a carbonaceous surface by heating [38]. Such adsorbents may dispose on higher adsorbing capacity than activated carbon and are non-abrasive. The expensive material is applied for gas masks and protection clothes [39].

Composite pore structures

The structure of porous material, natural or synthetic, is always complex. Although a tendency to produce materials of uniform texture can be observed, today most synthetic porous material exhibit a broad pore spectrum including composite pore structures. Already mention are 'gel pores' of cement paste. Another kind of secondary pore structure is often developed in regions in which the surfaces of primary particles approach each other, and come into contact. Also the section of a membrane filter prepared by drying of colloidal solutions of inorganic or organic particles exhibits a very complex system (Fig. 6 [16]).

The formation of the clay minerals by weathering processes is determined by the nature of the parent rock, climate, topography, vegetation, direction of movement of water through the weathering zone and the time period during which these factors operated. In the development of clay minerals by natural hydrothermal processes, the presence of alkalies and alkaline earths influences the resulting products. Near-neutral hydrothermal solutions bring about rock alteration, including the formation of illite, chlorite, and smectite, whereas acid hydrothermal solutions result in the formation of kaolinite.

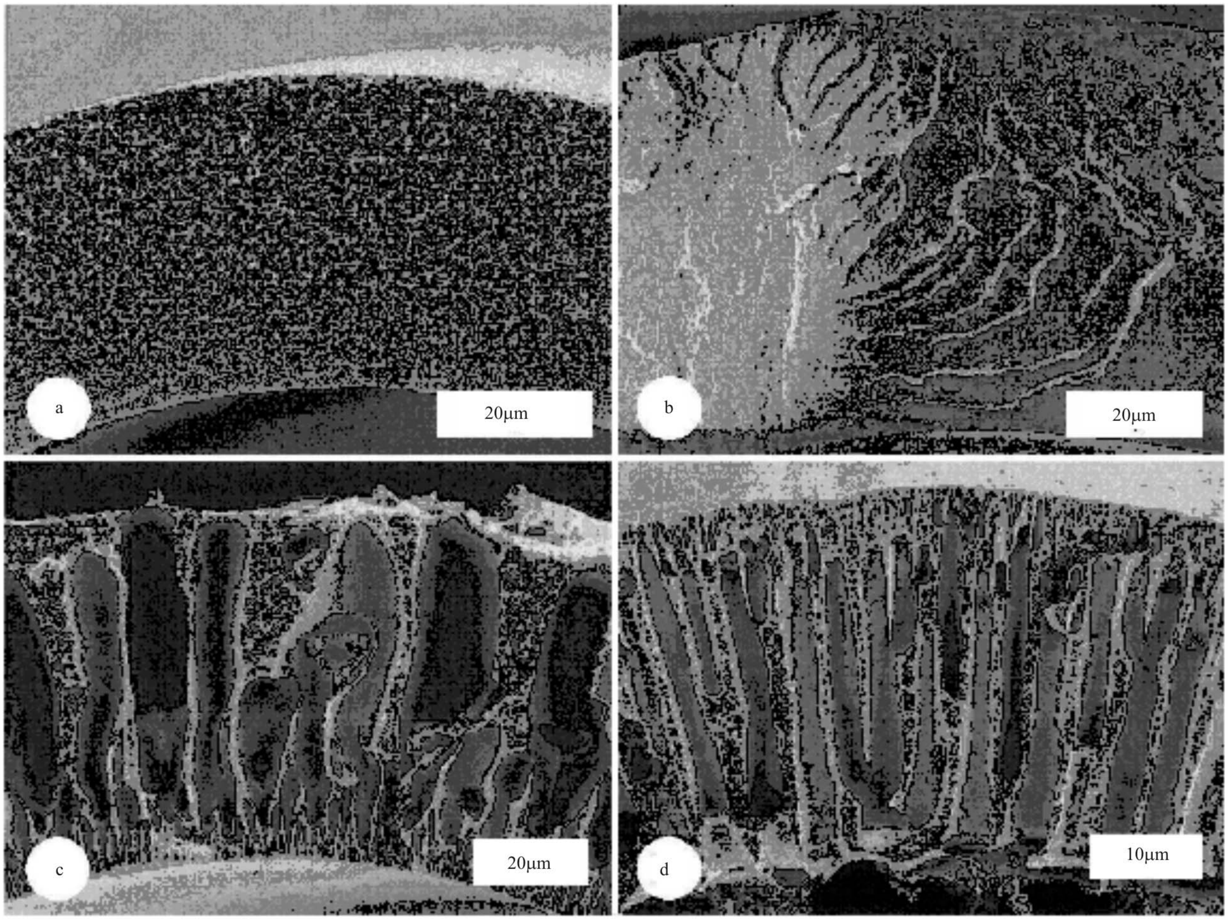

Fig. 6 SEM micrographs of the cross-section of the various refiltration membranes: a – FRES-2; b – HOS; c – GKSS-1; d – KSS-2

Mikhail [16] described a kind of secondary porosity which he called 'internal fuzz'. Electron micrographs indicate that crystalline material is often present, which is of orders of magnitude smaller than the effective pore diameters. This material may have the same chemical composition as the principal solid material or the composition may be different. An example gives the autoclaved slag-quartz-lime specimen shown in Fig. 7. Clay in sandstone or porous limestone may constitute fuzz in pores. Figure 8a to c, show some models for structures containing substructures. Neasham [40] pointed out that clay was formed hydrothermally in the sandstone, in a process that occurred long after the primary rock formation. In nature neoformation and transformation, are induced by weathering and hydrothermal actions.

Swelling

Binding forces may be well sufficient to exert stereologic changes of the surface or to separate weakly cohering particles. The pore structure of gel pores expands under the influence of certain liquids. Such liquids are in particular water and – in the case of organic matter – organic solvents [41]. In living matter water diffuses through cell membranes forced by osmotic pressure. Therefore, water can rise far above the hydrostatic level of about 10 m; some trees achieve a height of 120 m.

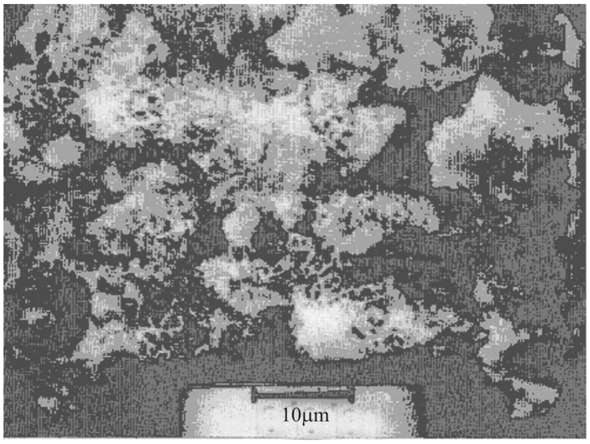

Fig. 7 SEM micrograph for slage-quartz-lime after 2 h autoclaving at 10 bar and saturated steam [14]

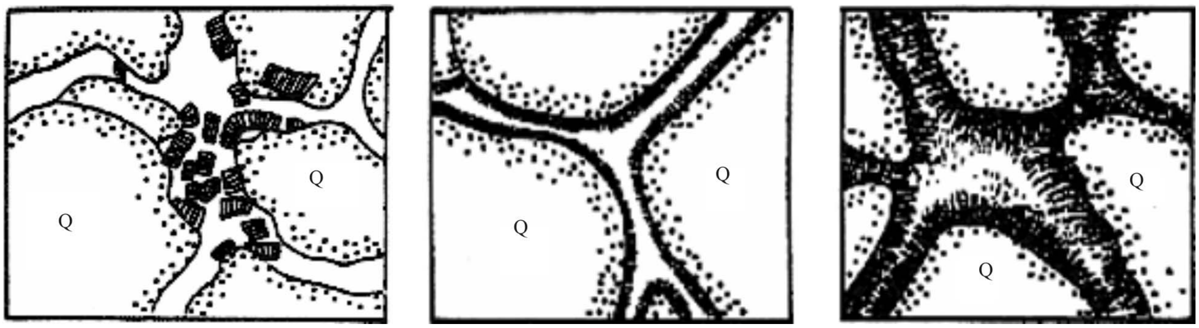

Fig. 8 Secondary clay sediments in sandstone schematical drawing, based on electron micrographs of J. W. Neasham , a – discrete particles of kaolinite, b – pore lining chlorite, c – pore bridging illite [37]

Swelling occurs in inanimate and living matter. It is an important means of biological organisms to form structures. Most plants can exist only when their cells are expanded by filling with water and whither when to much water is lost. Others – in particular in arid regions – shrink to reduce their outer surface and, hence, water evaporation and survive. Swelling effects are used by organisms to vary size and shape of organs and to carry out movements and even to move themselves. In many living organisms which reproduce sexually the respective organs swell in order to encourage or to enable sex. For that purpose cells are filled with additional water and/or blood vessels with additional blood.

If swelling is not desired, it can be reduced by fixation of the pore structure. Plants form rigid structures by lignifying. Animals form skeletons of a partly inorganic cellular structure. A technical example is the treatment of the cellulose fibres with formaldehyde resulting in acetal cross-links. In this way paper is stiffened. The pore structure can be frozen by forming an aerogel. If a porous material should be dried in many cases the pore structure collapses. This can be prevented by a freeze-drying procedure.

References

1 R. W. Seigel, In: R. W. Siegel, E. Hu and M. C. Roco, Eds, Nanostructure Science and Technology: A Worldwide Study, Loyola College, Maryland, 1999, p. 1.
2 Adsorption and Nanostructure, I. Dékány, Ed. Progress in Colloid and Polymer Science Vol. 117, Springer, Berlin 2001.
3 K. Beneke and G. Lagaly, In: G. Lagaly, Ed., ECGA Newsletter 2002, Reinhard Knof, Nehmten 2002, p. 57.
4 K. Beneke, Reinigungsmittel im Altertum., in Zur Geschichte der Grenzflächenerscheinungen – mit ausgesuchten Beispielen. Beiträge zur Geschichte der Kolloidwissenschaften, IV Mitteilungen der Kolloidgesellschaft., Reinhard Knof, Nehmten 1995, p. 56.
5 A. W. Adamson, Physical Chemistry of Surface, Fifth Edition, Wiley and Sons, 1990, p. 525.
6 A. Dąbrowski, Adv. Coll. Interface Sci., 93 (2001) 135.
7 E. Robens, Some intriguing items in the history of adsorption, In: R. J. Rouquerol, K. S. W. Sing and K. K. Unger, Ed., Characterization of Porous Solids III., Elsevier, Amsterdam 1994, p. 10.
8 A. Sayari and M. Jaroniec, Eds, Nanoporous Materials III. Elsevier, Amsterdam 2003.
9 K. Kaneko, T. Ohba, Y. Hattori, M. Sunaga, H. Tanaka and H. Kanoh, Role of gas adsorption in nanopore characterization. In: F. Rodriguez-Reinoso *et al.*, Eds, Characterization of Porous Solids VI, Elsevier, Amsterdam 2002, p. 11.
10 B. Coasne, A. Grosman, C. Ortega and R. J. M. Pellenq, Physisorption in nanopores of various sizes and shapes: a Grand Canonical Monte Carlo simulation study. In: F. Rodriguez-Reinoso *et al.*, Ed., Characterization of Porous Solids VI., Elsevier, Amsterdam 2002, p. 35.
11 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, Pure Appl. Chem., 57 (1985) 603.
12 M. J. Setzer, Zement und Beton, 85/86 (1975) 29.
13 H. Gräf and J. Bonzel, Zement und Beton, 85/86 (1990) 29.
14 M. M. Dubinin, Progress Surf. Membrane Sci., 9 (1975) 1.
15 DIN 66160: Messen disperser Systeme - Begriffe., Beuth, Berlin 1990.
16 R. S. Mikhail and E. Robens, Microstructure and Thermal Analysis of Solid Surfaces, Wiley and Sons, Chichester 1983.
17 E. Robens, Einiges zur Entstehung poröser Stoffe. In: R. Staudt, Ed., Technische Sorptionsprozesse, VDI Verlag, Düsseldorf 1998.
18 J. F. Byrne and H. Marsh, Origin and structure of porosity. In: J. W. Patrick. Ed., Porosity in Carbons, Edward Arnold, London 1995, p. 1.
19 J. Yang, J. M. F. Ferreira and W. Weng, Composite fine particles. In: A. T. Hubbard, Ed., Encyclopedia of Surface and Colloid Science, Vol. 1, Marcel Dekker Inc., 2002, p. 1118.
20 F. Vergnon, M. Aster and S. J. Teichner, Materials Science Res., 6 (1972) 301.
21 J. S. Hardmann and B. A. Lilley, Proc. Roy. Soc. London, A, 333 (1973) 183.
22 G. C. Bye and K. S. W. Sing, In: A. L. Smith, Ed., Particle Growth in Suspensions, Academic Press, London 1973, p. 29.

23 T. C. Powers, Chemistry of Cement, Proc. of the 4th Int. Conf. on the Chemistry of Cement, Washington DC 1960, p. 577.

24 E. Robens, B. Benzler, H. Reichert and K. K. Unger, J. Therm. Anal. Cal., 62 (2000) 435.

25 B. Subotić, Nucleation and crystal growth in zeolite systems. In: A. T. Hubbard, Ed., Encyclopedia of Surface and Colloid Science, Vol. 3, Marcel Dekker, Inc., 2002, p. 4255.

26 E. Robens, H. Heide and G. Walter, GIT Fachz. Lab., 27 (1983) 256.

27 C. Baerlocher, W. M. Meier and D. H. Olson, Atlas of Zeolite Framework Types, Elsevier, Amsterdam 2001.

28 www.IZA-structure.org/database.

29 www.members.AOL.com/Vbetz/zeolites.

30 UOP, An Introduction to Zeolite Molecular Sieves. 2000, Des Plaines: Universal Oil Products.

31 U. Müller, A. Tissler and K. K. Unger, GIT Fachz. Lab., 32 (1988) 635.

32 K. Eguchi, Hyomen, 25 (1987) 184.

33 H. Behret, H. Binder and E. Robens, Thermochim. Acta, 24 (1987) 407.

34 Nanotube, Nanotube Inc., Houston TX, USA. Frankfurter Allgemeine Zeitung, 242 (2000) p. N1.

35 R. T. Yang, Adsorbents: Fundamentals and Applications, Wiley-InterScience, New Jersey 2003, p. 79.

36 O. P. Krivoruchko, N. I. Maksimova, V. I. Zaikovskii and A. N. Salanov, Carbon, 38 (2000) 1075.

37 Rohm and Haas, Amberlite XAD Polymeric Adsorbents. Pharma 006., Rohm & Haas, Philadelphia 2000.

38 A. Dąbrowski, M. Bülow, Z. Hubicki and E. Robens, Role of Interfaces in Environmental Protection. In: S. Barany, Ed., NATO Sciencies Series 2003, p. 223.

39 R. Hike, W. Albrecht, Th. Weigel, D. Paul and J. Hapke, J. Membr. Sci., 166 (2000) 85.

40 J. W. Neasham, 52nd Annual Fal Technical Conference of the Society of Petroleum Engineers of AIME Denver CO., 1977.

41 C. J. Brinker and G. W. Sherer, Sol-Gel Science, Academic Press, New York 1990.