1
Concepts and Definitions

I. CLASSIFICATION OF PORES

A. Methods of Classifications of Pores

The notion of *pore* usually means a void inside a solid structure, especially if this void is connected to the surface. Pores and related porous structures can be classified according to [1]

1. Their characteristic size
2. Their connections to the surface
3. Their regularity of randomness
4. Their homogeneity or heterogeneity

Now, let us consider all above classifications.

B. Classification by the Characteristic Size of Pores

According to IUPAC [2], pores are classified by their size. Pores having size over 500 Å (50 nm) are defined as *macropores*; pores with size from 20 to 500 Angstrom (Å), *mesopores*; and pores with size below 20 Å, *micropores* [2]. Soviet researcher Dubinin recommended subdividing micropores into two groups usually termed *ultramicropores* (below 7 Å) and supermicropores (from 7 to 20 Å) [2–5]. The reasonability of such subdivision is related to the fact that ultramicropores have so specific properties as, for example, selective separation of molecules, and the energy of ultramicropores (per unit of volume) is enormous [2,6].

The IUPAC classification of pores would be very simple and logical if we were always able to measure pores, but that is the problem. Even macropores may have such varied shapes that the correctness of their size measurement (e.g., by using microscope) is too doubtable. For mesopores and especially micropores, observation of which is impossible without very precious electronic microscopes, the same problem seems absolutely critical. Nevertheless, we can introduce the notion of *characteristic size* that allows us to apply the IUPAC's definitions with the least logical error.

Since the shapes of pores can be absolutely various, it is very difficult to talk about pore size, radius, etc. However, we may assume that each pore is more or less characterized by its maximal size r_{max} (maximal distance between the closest opposite walls in the pore), minimal size r_{min} (minimal distance between the closest opposite walls in the pore), and the distribution of the internal surface (or internal volume) on the variable value of size. Let us assume that if a pore has $r_{max} > 500\,\text{Å}$ and $r_{min} < 500\,\text{Å}$, then it is not the entire pore but a combination of two (or more) pores. For example, a pore having $r_{max} = 1000\,\text{Å}$ and $r_{min} = 5\,\text{Å}$ can be divided into

Some macropores with $r_{max} = 1000\,\text{Å}$ and $r_{min} = 500\,\text{Å}$
Some mesopores with $r_{max} = 500\,\text{Å}$ and $r_{min} = 20\,\text{Å}$
Some supermicropores with $r_{max} = 20\,\text{Å}$ and $r_{min} = 7\,\text{Å}$
Some ultramicropores with $r_{max} = 7\,\text{Å}$ and $r_{min} = 5\,\text{Å}$

The above division allows us to consider separately all parts of the pore, applying the appropriate model to each of the parts.

Since the properties of macropores are determined by the internal surface, we define the characteristic size of macropores by the following equation:

$$r_c = \frac{\int_{r_{min}}^{r_{max}} r\rho(r)\,dr}{\int_{r_{min}}^{r_{max}} \rho(r)\,dr} \tag{1.1}$$

where the integral is taken over all the spectrum of countable values of r (from r_{min} to r_{max}) and $\rho(r)$ is the size distribution of the internal surface (surface area per volume unit for pore having the local size r).

Since the properties of mesopores are determined by both internal surface and internal volume, we define the characteristic size of mesopores by the following equation:

$$r_c = \sqrt{(r'r'')} \tag{1.2a}$$

$$r' = \frac{\int_{r_{\min}}^{r_{\max}} r v(r)\, dr}{\int_{r_{\min}}^{r_{\max}} v(r)\, dr} \tag{1.2b}$$

$$r'' = \frac{\int_{r_{\min}}^{r_{\max}} r \rho(r)\, dr}{\int_{r_{\min}}^{r_{\max}} \rho(r)\, dr} \tag{1.2c}$$

where $v(r)$ is the size distribution of the internal space (volume) in the mesopore (volume of pore having the local size r).

Since the properties of micropores are determined by their internal volume, we define the characteristic size of micropores by the following equation:

$$r_c = \frac{\int_{r_{\min}}^{r_{\max}} r v(r)\, dr}{\int_{r_{\min}}^{r_{\max}} v(r)\, dr} \tag{1.3}$$

Let us note that, according to the above definitions, the characteristic size of a mesopore is geometrically averaged between those of micropore and macropore.

Thus, the above definitions allow us to describe each pore with its characteristic size (or by the characteristic sizes of various parts of the pore).

C. Classification by the Connection to the Surface

According to this classification, a pore can be open, semiopen, or closed, depending on the connection to the surface of the porous sample (or different sides of the same sample).

An example of an open pore is given on Fig. 1.1.

As we can see from Fig. 1.1, the open pore is connected to both opposite sides of the solid sample. That means that this pore (this *open* pore)
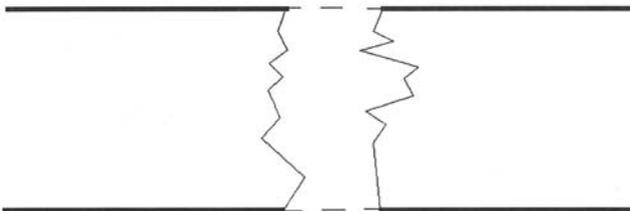

FIG. 1.1   Open pore in a solid sample.

can become a percolation path by which fluid fluxes can penetrate from the head side of the sample to its bottom side. If the open pore is ultra-micropore, it can realize the process of the selective separation.

Let us note that selective separation of components of fluids not only allows separation processes but sometimes makes possible carrying out of some reactions impossible in the same conditions without the separation. An example of such a reaction is the thermal decomposition of hydrogen sulfide with removal of hydrogen through microporous Vycor glass [7].

An example of a semiopen pore is given on Fig. 1.2.

As we can see from Fig. 1.2, the semiopen pore is connected to only one side of the solid sample. That means that this pore (this *semiopen* pore) cannot become a percolation path, but can participate in adsorptive processes. However, on the stage of desorption we may get a problem because the removal of the adsorbed substance from the semiopen pore needs more energy than in the case of an open pore. In such case, the pressure of the removal of the adsorbed substance from semiopen pore is over that of adsorption, and we obtain *hysteresis of adsorption–desorption loop*.

The problem of open and semiopen pores is related to the connectedness (also called *connectivity* or *interconnection*) of the porous structure. *Connectedness* means that the porous structure is continuous from one side of the porous solid sample to its opposite side. If the structure exhibits more tendency to connectedness, open pores predominate. On the contrary, in a porous structure with low connectedness open pores are not largely presented.

Closed pores have no connection to the pore surface. An example of a closed pore is given on Fig. 1.3.

As we can see from Fig. 1.3, the pore is isolated from both opposite sides of the solid sample. That means that this pore (this *closed* pore) cannot participate in mass transfer processes, comprising adsorption–desorption and percolation. However, the presence of closed pores reduces the density
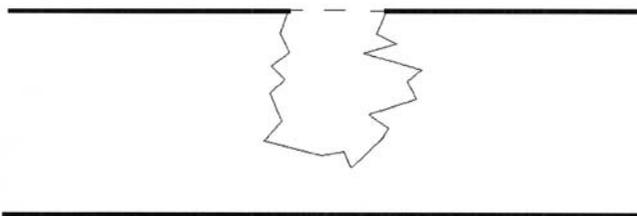

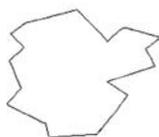**FIG. 1.2** Semiopen pore in a solid sample.

FIG. 1.3 Example of a closed pore inside a solid sample.

of the solid sample and increases its thermal, electrical, and acoustic insulation properties. Let us notice that closed pores (as all pores, of course) influence mechanical properties of the solid material, in most cases reducing the mechanical resistance of the solid sample.

As follows from the above, the classification by the connection to the surface is relative. At the same porous structure, the same porous fragments may provide open, semiopen, or closed pores depending on the manner of cutting the solid material into samples.

Let us note that we need pay more attention to the classification by the connection to the surface in the case (as we have considered above) if the same pore can be divided into macro-, meso-, and micropores. Such division, of course, cannot transform open pores into a combination of semiopen and closed pores. If a micropore is not connected to the surface but is connected to a semiopen or open meso- or macropore, that micropore can be, respectively, semiopen or open. Such a situation is largely spread in heterogeneous catalysts: macropores are connected to the surface (they are, respectively, open or semiopen) and allow the transportation of the reagent-containing fluids into micropores, while the micropores transport the reagents to the catalytic nuclei. When the initial reagents are consumed and the products formed, they are transported through micropores to macropores, through which the products are removed to the exterior surface of the catalyst.

The problem of the relativity of choosing the manner of cutting the porous solid sample will be discussed below when we will consider the problem of percolation and permeability (Chapter 4).

D. Classification by Regularity of Randomness

This classification is tightly related to the process of the synthesis of the porous material. A porous structure is called *regular* if it can be divided into a number of systematically repeating fragments. Two examples of regular porous structures are presented on Figs. 1.4 and 1.5.

A   A   A   A   A   A   A

A   A   A   A   A   A   A

A   A   A   A   A   A   A

A   A   A   A   A   A   A

A   A   A   A   A   A   A

A   A   A   A   A   A   A

FIG. 1.4 Porous structure with repeating fragment A: the location changes regularly, the shape does not change, and the size changes monotonically.

A   A   A   A   A   A   A

a   a   a   a   a   a   a

A   A   A   A   A   A   A

a   a   a   a   a   a   a

A   A   A   A   A   A   A

a   a   a   a   a   a   a

A   A   A   A   A   A   A

a   a   a   a   a   a   a

FIG. 1.5 Regular porous structure: repeating fragment "Aa" by location, shape, and size.

Based on Figs. 1.4 and 1.5, we can conclude that not only simple copying but also monotonic change in one of parameters (shape, location, and/or characteristic size) leads to the regularity in the porous structure.

Regular structures are not widespread among microporous materials. Most of these are randomly structured. A porous structure is called *random* if it is impossible to find a little (in comparison with the sample entire) fragment of the structure repeating systematically throughout the sample. An example of random porous structure is given on Fig. 1.6.

It is not a great fault to assume that only zeolites have regular porous structure. The problem of the formation of the regular structure of zeolite will be considered in Chapter 3.
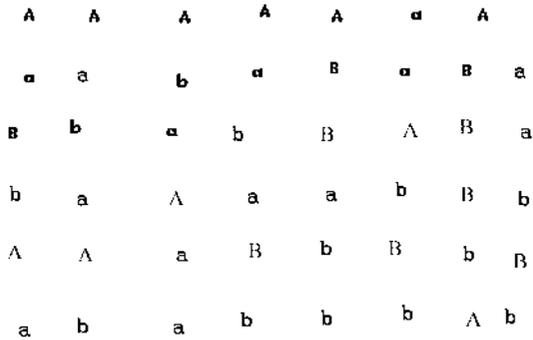
FIG. 1.6 Random porous structure: impossible to find any fragment repeating systematically throughout the structure.

E. Classification by Homogeneity or Heterogeneity

This classification is similar to that by regularity or randomness. We call a porous structure *homogeneous* if the averaged properties of all its fragments, sizes of which are much larger than those of pores, do not significantly differ. On the contrary, if such fragments differ significantly in properties (entropy per volume unit, internal energy per volume unit, chemical composition of the continuous phase, local porosity, size distribution of pores, etc.), the porous structure is called *inhomogeneous* or *heterogeneous*. We notice that the sense of homogeneity and heterogeneity is very relative, because pore itself is heterogeneous, since it contains interface continuous phase void.

Not every regular porous structure is homogeneous. For example, the structure presented on Fig. 1.5 is homogeneous, while that on Fig. 1.4 is heterogeneous. The random structure on Fig. 1.6 can be homogeneous because there is no obvious difference between various fragments, sizes of which are much larger than those of the pores.

II. MICROPORES AND DEFECTS IN CRYSTALS

Now, let us compare micropore to a very similar phenomenon, defect in crystalline structure [3,8–10]. Defect in crystal (dislocation) is understood as a void, eventual vanishing of a particle belonging to a crystalline structure from the spot at which the particle "should be found." Two examples of defects in crystals are given in Figs. 1.7 and 1.8.

Let us compare Fig. 1.7 to Fig. 1.2 and Fig. 1.8 to Fig. 1.3. The similarity between Figs. 1.7 and 1.8 and Figs. 1.2 and 1.3, respectively, is

```
A    X    A         A    X

X    A    X    A    X    A

A    X    A    X    A    X

X    Λ    X    A    X    Λ

A    X    Λ    X    A    X

X    A    X    Λ    X    Λ
```

FIG. 1.7   Defect on the surface of a crystalline structure.

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A    X    A    X    A    X

X    Λ    X    Λ    X    A

Λ    X    Λ         A    X

X    A    X    Λ    X    A

A    X    Λ    X    Λ    X

X    Λ    X    A    X    A
```

FIG. 1.8   Defect in the volume of a crystalline structure.

obvious. In Figs. 1.2 and 1.7 the void is connected to the surface, whereas in Figs. 1.3 and 1.8 the void is located inside the solid sample. Is it so important whether the sample is crystalline or amorphous? Is it so important whether the void is big or small? Moreover, there are some

specific crystals (zeolites) in which pores can give formation. The difference between micropore and crystalline defect may seem less important than the divergence between micropore and macropore.

The similarity between micropores and defects was discussed in the literature [11], and the physical difference between these phenomena needs serious analysis.

The comparative analysis (given below) aims to emphasize the physical difference between these two phenomena—micropores (comprising micropores in crystals) and defects in crystals.

1. The driving force for micropore formation and defect formation in crystal is the same, that is, the increase of entropy, whereas the total internal energy gets rising too. Hence, the thermodynamics of micropore and defect formation is very similar (but not identical—see below).

2. The mechanism of micropore and crystal defect formation is absolutely different. Micropores are formed due to removal of gas or vapor because of chemical decomposition of the material in which micropores are formed, and this process of gas–vapor particle removal is definitely irreversible. On the contrary, defects in crystals are formed due to statistical fluctuations, and the particles dislocated from their positions inside crystals do not get removed away but remain inside the crystalline structure or on the surface, and the process of defect formation is reversible. Thus, micropore formation is described by thermodynamics of non-equilibrium, while defect formation is described by thermodynamics of equilibrium.

3. Both micropores and defects can be formed in zeolites (regular crystalline structures formed by cocrystallization of some metal-oxide hydrates with further careful removal of water). However,
   a. Micropores in zeolites are formed due to removal of water (irreversible process, as analyzed above in item 2).
   b. Defects in the same zeolites are formed due to eventual removal or dislocations of ions belonging to the regular structure, and this process is reversible in principle (as above given in the general case by item 2).

4. Motion inside the solid structure is possible for particles in crystals but forbidden for particles around micropores. Micropores cannot move inside the solid (continuous) structure, unless this is destroyed. Defects can easily move, that is one of sequences of the reversibility of defect formation. Inside a crystalline structure,

TABLE 1.1 Comparison of Micropores with Crystal Defects

Factor of comparison	Micropore	Defect in crystal
Driving force for formation	Increase of entropy	Increase of entropy
Change of internal energy	Increase	Increase
Possible in nonzeolite crystals?	Negative	Positive
Possible in amorphous structures?	Positive	Negative
Possible in zeolites?	Positive	Positive
Formation is reversible?	Negative	Positive
Motion is possible?	Negative	Positive
Continuous growth is possible?	Positive	Negative

       an ion can come into the vacant spot of the defect just due to heat vibrations; then the defect disappears at its previous position but appears at a new position.

5.   Continuous growth of micropores is not only possible but very probable if the conditions necessary for the micropore formation take place. On the contrary, defects in crystals cannot get continuous growth (unless the crystal is destroyed), because the eventual neighborhood of two or more defects is the low-probability option.

The comparison of micropores to crystal defects is illustrated by Table 1.1.

III. RELATIONSHIP BETWEEN THE SYNTHESIS OF POROUS MATERIALS AND CHARACTERISTICS OF THEIR STRUCTURES

The following analysis regarding the relationship between the conditions of pore formation and the properties of the resulting porous structure is just qualitative. The numerical analysis is not given in this chapter but will be presented later.

      Macropores are formed mostly because of mechanical treatment of solid materials, whereas micropores are formed due to chemical reactions in certain conditions. However, macropore formation due to mechanical effects is always accompanied by the eventual appearance of nanopores—mesopores and micropores in the zones where the mechanical destruction is minor. Micropore formation due to chemical reactions cannot, except few situations, be realized without eventual formation of macropores (see Fig. 1.9).
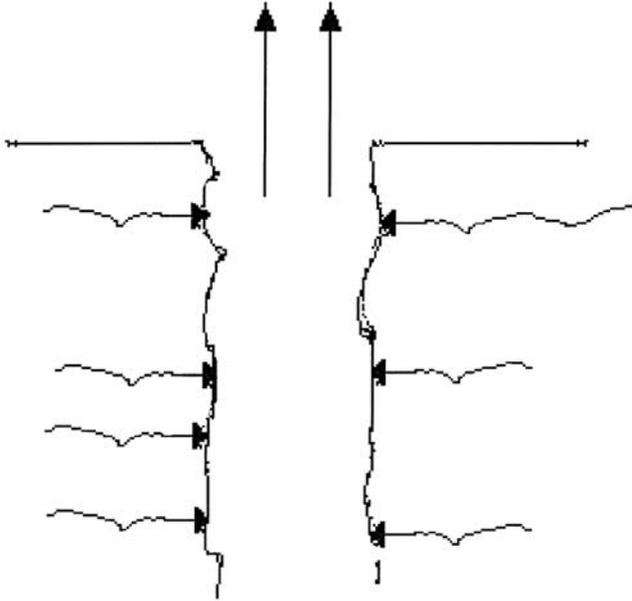
FIG. 1.9 Simultaneous formation of micropores and mesopores or macropores due to chemical reactions inside the solid phase.

Of course, both chemical reactions and mechanical effects cause also formation of mesopores.

All factors related to preparation (synthesis) of porous materials can be divided into two groups:

Characteristics of the raw materials
Parameters of the process of the treatment of the raw materials

We can divide all processes of pore formation in solids into two groups:

1. Pore formation in a solid material previously prepared (which means the solid is prepared *before* being treated for getting pores)
2. Pore formation simultaneously with the preparation of the solid material (which means the processes of synthesis of the solid and its treatment for pore formation are carried out in the same time, in the same volume)

For pore structure formation, one can use all existing amorphous solids. For pore formation simultaneously with the solid formation (synthesis), one can use all known physicochemical processes providing

solid phase, such as separation of hydrocarbon mixtures, partial oxidation of hydrocarbons (in liquid or gaseous phase), polymerization, sedimentation, etc.

Among the properties of solid raw materials influencing pore formation we note the following:

1. Polymeric or nonpolymeric structure of the raw material (if polymeric, its structural characteristics comprising branching, cross-linking, etc.)
2. Mechanical properties of the raw material (its mechanical resistance, elasticity, etc.)
3. The content of volatile and unstable components (means first of all, organic groups)
4. The surface tension of the solid phase contacting with air

Polymeric structure of the raw (solid) material is favorable for the formation of micropores more than macropores under the same exterior conditions because natural interactions between neighbor momomeric units stimulate the formation of micropores. For the same reason, among polymeric materials, cross-linked structure with intense branching (first of all rubbers) is very favorable for micropores, but the total porosity decreases.

The high mechanical resistance and high elasticity allow very large freedom of choice for the researcher in varying exterior effects for getting a porous structure. Even if the micropores are formed by reactions inside the solid phase, the large elasticity allows the removal of volatile components with minimal formation of macropores. On the contrary, low elasticity and low mechanical resistance are factors very favorable for the local destruction of the solid phase and, as sequence, formation of macropores. In principle, this process may result even in breaking the solid phase.

The moderate content of volatile components is especially important for the intense micropore formation. If their concentration is low, micropores are rare, isolated, short, and semi open or closed. If volatile components are very abundant, the experiment needs to be very carefully controlled, in order to prevent too deep a decomposition of the solid (otherwise, the materials may be locally broken).

Let us notice that in processes of micropore preparation by decomposition of solid materials, the chemical composition and properties of the solid products may significantly differ from those of the raw materials. In such cases,

1. The kind of the resulting solid structure (polymeric or non-polymeric) remains important.

2. Mechanical properties of the resulting solid are not so important, unless that is related to its further use.
3. The rest content of the volatile components is not important, unless needed for the further use.
4. That is very important to evaluate the surface tension of the resulting solid phase in contact with the gas or the vapor that is expected inside the micropores at the moment of their formation (σ). We note that *the measurements of σ do not need intervention inside micropores*. Instead, it is sufficient to measure the same parameter in standard laboratory conditions for the plate solid surface (having zero curvature) in the atmosphere of the same gas or vapor.

A. Parameters of the Treatment Process

Pore formation is influenced by the following characteristics of the treatment process:

All intensive parameters: pressure P (Pa), temperature T (K), mechanical tension P_m (Pa), concentrations of reagents C_i (mole parts), etc.

Gradients of the intensive parameters and changes of these parameters with time t (s)

Various initiating rays

The total duration of the treatment t_t

The pressure and/or tension loading, especially by vibration, stimulates not only formation of macropores but also transformation of micropores to macropores. If the vibration duration is too long, the solid sample is just destroyed.

The pressure unloading stimulates delivering of volatile components, particularly water vapor. The same effect is obtained if not the total pressure but the partial pressure of water vapor is reduced. In both cases, the obtained structure is mostly microporous, whereas the micropores are open or semiopen. The resulting structure cannot be regular unless it was initially, i.e., before the treatment (e.g., dehydration of zeolites). The porous structure is homogeneous if the treatment was careful and homogeneous: all fragments of the solid phase are under the same intensive parameters (of course, this condition does not work at the border of the condensed phase).

The temperature can influence pore formation in two directions:

1. Temperature rising causes thermal enlargement of the solid phase; if this is heterogeneous, its different parts get different

enlargements, that is, equivalent to mechanical tension, and, respectively, favors the formation of macropores.

2. Temperature rising may stimulate chemical reactions, first of all endothermic decomposition and oxidation of organic components, with delivery of volatile products (water vapor, carbon dioxide, nitrogen, etc.), that is favorable for micropore formation.

Thus, the sequences of thermal treatment of solid are ambivalent and depend on the structure and the chemical composition of the treated solid material.

As it will be shown in the further analysis, the dynamics of temperature changing with time influences significantly the resulting microporous structure, but that is a very specific phenomenon, analysis of which stands out of this chapter.

Initiating rays [ultraviolet (UV), x-rays, acoustic waves like ultrasound, etc.] may cause radical formation. The free radicals attack the unstable organic components in the solid phase, and the result is similar to that in the case of the thermal oxidation or decomposition. However, the ray-initiated chemical reactions have a very serious advantage: in the case of the ray treatment of a heterogeneous solid, macropore formation in which is not desired (e.g., oxidation of pollutants adsorbed on active carbon), macropores almost do not get be formed.

The total duration of the treatment, even without changing the regime of the treatment (e.g., long time heating of the raw material), leads to deep changes in the solid structures. In many cases, this can cause

1. Increase of the total porosity
2. Transformation of micropores and mesopores to macropores
3. Breaking of the solid

The principal sequences of the treatment of organic-containing solids with the above-considered technique are given in Tables 1.2 to 1.5.

Comparing Tables 1.2 and 1.3 to Tables 1.4 and 1.5, respectively, we find that the results of the treatment of similar (in the chemical composition) materials are very similar but not identical, and the initial structure of the raw solid material is extremely important.

B. Effect of Exterior Treatment on the Pore Formation in Processes of Synthesis of Solid

We mentioned above the following processes most important for the synthesis of porous solid from gaseous or liquid raw materials: separation of hydrocarbon mixtures, partial oxidation of hydrocarbons (in liquid or

TABLE 1.2 Structure Formation in Process of the Treatment of Carbon

Characteristics of the resulting structure	Pressure, mechanical tension	Temperature increase	Destroying agents plus initiating rays
Micropore formation	Negligible[e]	Yes[a]	Yes
Mesopore formation	Minor[d]	Yes	Yes
Macropore formation	Very possible[b]	Yes	Minor
Cracking or breaking of the solid	Very possible	Possible[c]	No
Open pores	Yes	Possible	Yes
Semiopen pores	Yes	Yes	Yes
Closed pores	No[f]	Possible	No
Random porous structure	Yes	Yes	Very possible
Regular porous structure	No	No	Minor
Heterogeneous structure	Possible	Very possible	Very possible
Homogeneous structure	Possible	Minor	Minor

[a]Yes means the effect is doubtless.
[b]Very possible means the effect is very probable.
[c]Possible means the probability of the effect is moderate.
[d]Minor means the probability of the effect is low.
[e]Negligible means the probability of the effect is very low.
[f]No means the effect should not appear.

gaseous phase), polymerization and, sedimentation. Let us give some examples of these processes.

1. Separation of Hydrocarbons

Such a known and widespread process as petroleum refining comprises, as one of its sequences, delivering a very hard fraction of hydrocarbons— bitum used as the raw material for asphalt. This consists of a mixture of hard hydrocarbons forming a porous solid phase. The usual synthesis of such a porous product comprises the following stages: condensation, separation from light and intermediary fractions, cooling and keeping as solid, then (for use as asphalt) heated, put onto the chosen surface, and naturally cooled. Asphalt contains all kinds of pores. Many pores are open; this fact makes the removal of water during rains easier.

2. Oxidation of Hydrocarbons and Organics

This technique is used for the synthesis of active carbon. Primary materials (waste organics) are carefully oxidized under high temperature, which causes formation of all kinds of pores, while micropores dominate.

TABLE 1.3 Structure Formation in Process of the Treatment of Polymeric Solid

Characteristics of the resulting structure	Pressure, mechanical tension	Temperature increase	Destroying agents plus initiating rays
Micropore formation	Minor[d]	Yes[a]	Yes
Mesopore formation	Minor	Yes	Yes
Macropore formation	Very possible[b]	Possible[c]	No[e]
Cracking or breaking of the solid	Very possible	No	No
Open pores	Yes	Very possible	Yes
Semiopen pores	Yes	Yes	Yes
Closed pores	No	Possible	No
Random porous structure	Yes	Yes	Very possible
Regular porous structure	No	No	Minor
Heterogeneous structure	Possible	Very possible	Very possible
Homogeneous structure	Possible	Minor	Minor

[a]Yes means the effect is doubtless.
[b]Very possible means the effect is very probable.
[c]Possible means the probability of the effect is moderate.
[d]Minor means the probability of the effect is low.
[e]No means the effect should not appear.

In the general case, the obtained structure is random. However, several studies show the principal opportunity of the synthesis of active carbon, the structure of which is characterized by several regularities (see, e.g., Ref. 12). Such molecular sieving carbons with uniform micropore structure are prepared by (1) carbonization of metal-cation-exchanged resin and (2) pyrolytic carbon deposition from benzene over activated carbon fibers. Both micro- and mesoporosity are under control. High-performance molecular sieving carbon membranes for gas separation are synthesized from the carbonization of several types of organic polymer films. Mesopores are controlled by such novel methods as catalytic activation, polymer blend carbonization, organic gel carbonization, and template carbonization [12].

3. Polymerization

Most of reactions of polymerization (radical or ionic) lead to the formation of microporous solids. Macropores appear mostly in specific processes—e.g., foam synthesis with gas injection into the polymerizing phase—and are always accompanied by micropore formation. Macropores and mesopores take much less volume fraction. The simplest linear polymerization is

TABLE 1.4 Structure Formation in Process of the Treatment of Zeolites

Characteristics of the resulting structure	Pressure, mechanical tension	Temperature increase	Reduction of partial pressure of water vapor
Micropore formation	Negligible[e]	Yes[a]	Yes
Mesopore formation	Minor[d]	Yes	Yes
Macropore formation	Minor	Minor	Minor
Cracking or breaking of the solid	Yes	Yes	No
Open pores	No[f]	Minor	Possible[c]
Semi-open pores	Minor	Yes	Yes
Closed pores	No	Possible	No
Random porous structure	Yes	Yes	Minor
Regular porous structure	No	No	Yes
Heterogeneous structure	Possible	Very possible[b]	Minor
Homogeneous structure	Possible	Minor	Yes

[a]Yes means the effect is doubtless.
[b]Very possible means the effect is very probable.
[c]Possible means the probability of the effect is moderate.
[d]Minor means the probability of the effect is low.
[e]Negligible means the probability of the effect is very low.
[f]No means the effect should not appear.

favorable for the formation of open and semiopen micropores and (much less) open mesopores. Branched polymerization increases the fraction of micropores, while the tendency of the formation of semiopen pores dominates. Cross-linking in macromolecules reduces the porosity and stimulates closing pores. In any case, the product has random porous structure. In a normal situation, the polymer is homogeneous, but if necessary, the polymerization can provide heterogeneous products (e.g., due to using block polymers or composites).

4. Sedimentation

Processes of sedimentation can be carried out in very different conditions. If solid particles are allowed to move down due to simple gravitation, the obtained solid structure is microporous. In many cases, the products of sedimentation (e.g., silica gel or alumina gel) get secondary treatment, mainly thermal. The changes of the porous structure during the secondary treatment do not differ from those described in Tables 1.2 to 1.5. If the rate of sedimentation is increased, e.g., by centrifugation, the porosity decreases, the characteristic size of micropores decreases, and the obtained pores are semiopen or closed. The resulting porous structure is random and is not

TABLE 1.5 Structure Formation in Process of the Treatment of Silica–Alumina Gel

Characteristics of the resulting structure	Pressure, mechanical tension	Temperature increase	Reduction of partial pressure of water vapor
Micropore formation	Negligible[e]	Yes[a]	Yes
Mesopore formation	Minor[d]	Yes	Yes
Macropore formation	Minor	Possible[c]	Minor
Cracking or breaking of the solid	Yes	Minor	No[f]
Open pores	No	Very possible[b]	Possible
Semiopen pores	Minor	Yes	Yes
Closed pores	No	Yes	No
Random porous structure	Yes	Yes	Minor
Regular porous structure	No	No	Yes
Heterogeneous structure	Possible	Very possible	Minor
Homogeneous structure	Possible	Minor	Yes

[a]Yes means the effect is doubtless.
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[c]Possible means the probability of the effect is moderate.
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[e]Negligible means the probability of the effect is very low.
[f]No means the effect should not appear.

homogeneous but has the cone symmetry: heterogeneity is found by the vertical (because of the gravitation), whereas by the horizontal the structure is homogeneous (see Fig. 1.10).

A specific situation takes place when sedimentation is not carried out by simple gravitation but is realized in the regime of crystallization. In most of cases, such situation does not regard pore formation. However, if the obtained crystals contain water, this can be sometimes carefully removed by increasing temperature and/or reducing the partial pressure of water vapor, obtaining molecular sieves, zeolites.

We note that since micropores are formed mainly due to chemical reactions, the notion of *synthesis* seems well applicable to micropore formation, though that is not synthesis in the traditional sense (as is understood in inorganic and organic chemistry). This term allows us to emphasize the physical difference between micropore formation (due to chemical reactions) and macropore formation (mostly due to mechanical effects). Moreover, in the situation when micropores are formed simultaneously with the solid phase, the notion of *synthesis of micropores* becomes logically valid even in the traditional sense.

FIG. 1.10 Horizontal homogeneity and vertical heterogeneity in porous structure after simple sedimentation.

C. Influence of the Treatment on the Homogeneity and Heterogeneity of Porous Structure

Since the porous structure is determined by both raw material and the regime of its treatment, homogeneous porous structure can be obtained in one of the following situations:

1. The raw material is initially homogeneous and gets the homogeneous treatment. The homogeneity of the treatment means that all fragments of the raw material get mechanical, chemical, and/or thermal treatment and/or initiating irradiation at the same intensive parameters (pressure, temperature, concentrations of chemical reagents, wavelength) at the same duration. An example of such a process is transformation of alumosilicate hydrates to zeolites.

2. The raw material is initially heterogeneous, but its treatment is homogeneous and so intense that the initial heterogeneity is neutralized. An example of such a process is the recovery of active carbon from the products of the adsorption of organic pollutants with active carbon (the organic pollutants are oxidized and not only deliver the active carbon but, moreover, form some additional amount of active carbon). Though such raw material

was initially heterogeneous, the careful treatment allows its transformation to homogeneous, pure active carbon.

D. Open, Semiopen, and Closed Pores

The pore opening and closing are very specific characteristics that do not significantly depend on the raw material. Their dependence on the parameters of the treatment process is significant but not decisive. Much more important for pore opening and closing is the manner of the sample preparation. If the ready porous material is cut to thin films (membranes), these contain mostly open pores. Such a procedure can be especially important in the preparation of microporous membranes of zeolites, several polymers, and composites or silica gel: most of their micropores get opening. That transforms these films, due to selective properties of ultramicropores, to a powerful technique for precious separation processes (of course, in the case of zeolites the micropores remain regular, while in other mentioned materials they remain random). However, since opening pores is very significant for heat or mass transfer through porous structures, it is very commendable to pay attention to some technologies allowing preparation of microporous structures with high tendency to opening. Let us give some examples of such processes.

(a) *Example 1.1.* Microporous ceramic materials having an open microporous cell structure with an internal surface area $>50 \, \text{m}^2/\text{g}$ (microporous structure comprises a volume fraction above $0.015 \, \text{cm}^3/\text{g}$ of the ceramic) can be synthesized on the base of nonsilicon containing ceramics, carbon, and inorganic compounds having a decomposition temperature over $400°C$ [13].

(b) *Example 1.2.* Microporous ceramic materials having an open microporous cell structure with an internal surface area $>70 \, \text{m}^2/\text{g}$ (microporous structure comprises a volume fraction above $0.03 \, \text{cm}^3/\text{g}$ of the ceramic) can be synthesized on the base of silicon carbide, silicon nitride, and silicon–carbide–nitride ceramics [13].

(c) *Example 1.3.* A porous material having open pores can be prepared by casting a slurry from a mixture containing a bisphenol-type epoxy resin, an amide compound as a hardener, a filler, and water in a water-impermeable mold, hardening the slurry while it contains the water, further dehydrating the hardened article. The mean pore size estimated 4.0 nm, and the apparent porosity can be up to 41% [14].

(d) *Example 1.4.* An aluminum-oxide-based ceramic catalyst support with open interconnecting pores can be prepared by mixing fine-grained

aluminum oxide with bonding clay, organic binding agents, and water to form a suspension. This is added to a polystyrene framework formed by treating polystyrene balls with aqueous acetone. The aluminum oxide and the supporting polystyrene framework are dried, the polystyrene is removed by heating, and the aluminum oxide support containing open interconnecting pores is sintered at 1600°C for 2 h. The aluminum oxide support is used with a nickel-based catalyst [15].

(e)   Example 1.5.   Chen et al. [16] noticed that, in many applications, usefulness of conventional hydrogels was limited by their slow swelling. To improve the swelling property of the conventional hydrogels, Chen et al. [16] have synthesized superporous hydrogels (SPHs) that swell to equilibrium size in minutes due to water uptake by capillary wetting through numerous interconnected open pores. The swelling ratio was also large in the range of hundreds. The mechanical strength of the highly swollen SPHs was increased by adding a composite material during the synthesis. The composite material used in the synthesis of SPH composites was Ac-Di-Sol(R) (croscarmellose sodium). Their study indicated that SPH composites possessed three required properties: fast swelling, superswelling, and high mechanical strength [16].

The results of the analysis of the relationship between the characteristics of the simultaneous synthesis of microporous structure with the solid phase itself and the characteristics of the porous structure are given in Table 1.6.

TABLE 1.6   Influence of the Parameters of the Process of Synthesis of Porous Solid onto the Characteristics of the Porous Phase[a]

Technique of treatment	Main pore size	Opening and closing pores	Homogeneous or heterogeneous[b]
Polymerization:			
Linear	Micropores, mesopores	Open	Homogeneous
Branched	Micropores	Open, semiopen	Homogeneous
Cross-linked	Micropores	Semiopen, closed	Homogeneous
Oxidation of organics	Micropores, mesopores	Open, semiopen	Homogeneous
Sedimentation (by gravitation)	Micropores	Open, semiopen	Heterogeneous (cone symmetry)

[a]Note: the column regularity or randomness is not included into the table because *all* known structures prepared simultaneously (solid + pores) are random only.
[b]Assume the condition that the synthesis process is homogeneous in the sense claimed above.

IV. RELATIONSHIP BETWEEN THE POROUS STRUCTURE OF A SOLID MATERIAL AND ITS PROPERTIES HAVING TECHNICAL MERIT

As in the previous article, the below analysis of the relationship between the structure of a porous material and its measurable properties is just qualitative. The mathematical models and the numerical studies of microporosity will be presented in Chapters 3 to 5.

Among numerous interesting properties of porous materials, in the further analysis we will deal with

1. Specific properties of porous materials that are not found for nonporous materials
2. Specific properties of porous materials finding technical and/or domestic applications

In the Preface to this book, we gave a list of technically important specific properties of porous materials: heat, electrical, or acoustic isolation, adsorption of various substances (and, as sequences, catalytic properties and such uses as fluid component separation and poison removal), percolation and permeability (as their sequence, fine selective separation of components of fluids), and regulated mechanical properties.

Now, let us consider the influence of various qualitative characteristics of porous structure on the above measurable properties.

A. Insulation Properties

The large size of a pore seems very favorable for the insulation properties of a porous material. However, the most important is the total porosity (of course, many little pores over the volume of the solid sample provide much better insulation than one big pore, the volume of which is less than the total volume of the mentioned little pores). At the same value of porosity, better insulation is found for microporous materials, because micropores constrain mass transfer and heat transfer, respectively, by convection. Open pores do not allow enough good insulation, because allow convective heat transfer [17]. Open pores allow also percolation [18] that harms the acoustic and electric insulation. Semiopen pores cancel percolation and seriously reduce convective heat transfer. However, only closed pores make convective heat transfer negligible (which can exist just because of the motion of the interior gas inside the closed pores). Moreover, in a closed micropore such motion is practically impossible, and the closed microporous structure is the best insulator in comparison with alternative structures. Regular and random porous structures do not significantly differ

in the aspect of insulation properties, and their divergence can be estimated only on the stage of mathematical models. Heterogeneous structures provide weaker insulation because the limiting rate of heat or mass transfer is determined by the maximal available local rate, which is larger on the zones of low local porosity, whereas the homogeneous structures have equal local thermal, mass transfer, and electrical resistance.

B. Adsorption and Heterogeneous Catalysis

Adsorption is understood as ''capturing'' several substances (component of gas or liquid phase) by solid surface (exterior or interior), mostly micropores. Let us compare adsorption to absorption—capturing of substance by liquid or (very rarely) solid volume. We notify that since adsorption in micropores is due to their active volume, microporous adsorption has some features of absorption (see Table 1.7).

We can deduce that adsorption by micropores can be considered as a phenomenon intermediary between the traditional adsorption and absorption.

Let us note that *desorption* is usually understood as the process reverse to adsorption; however, to avoid misunderstanding, one needs to remember that *desorption* means also the process reverse to absorption. Thus, *desorption* can be defined as the process of delivering of captured substance from the condensed phase, but the exact sense of desorption becomes clear only after determining the mechanism of the process precedent to desorption—absorption or desorption.

Now, let us consider some examples of adsorption and heterogeneous catalysis on porous adsorbents.

(a) Example 1.6. The adsorption of mainly butyl and heptyl alcohols from water solutions by means of six different charcoals ranging widely in pore size was investigated by Dzhigit et al. [19] to show the effect of the pore structure onto the limited adsorption of alcohols of limited solubility in water. It was shown that the charcoal structure was having a strong effect on the shape of the adsorption isotherms and on the values of the limit adsorption. The rule of constant adsorbed limit volumes was found approximately true for each of the carbons adsorbing one of four alcohols (from butyl to heptyl). It was notified that the micropores of the charcoals are equally accessible to the different alcohols and densely filled by the alcohol molecules at limit adsorption [19].

(b) Example 1.7 (water purification). Active carbons for water treatment can be obtained by steam activation of olive-waste cakes. This raw material is an abundant and cheap waste by-product of oil production that

TABLE 1.7 Comparison of Adsorption in Micropores to Adsorption in Mesopores and Macropores and Absorption

Factor of comparison	Adsorption on plate surface or macropore	Adsorption in mesopores	Adsorption in micropores	Absorption in liquid	Absorption in solid[a]
Driving force of the process	Decrease of internal energy	Decrease of internal energy	Decrease of internal energy	Decrease of internal energy	Decrease of internal energy
Sorption by surface	Yes	Yes	No	No	No
Sorption by volume	No	Yes	Yes	Yes	Yes
Capturing by solid phase	Not relevant	Not relevant	Not relevant	No	Yes
Capturing by liquid phase	Not relevant	Not relevant	Not relevant	Yes	No
Capturing by continuous phase	No	No	No	Yes	Yes
Transport of captured substance through all the continuous phase	No	No	No	Yes	Yes

[a]An example of absorption by solid: absorption of hydrogen by platinum.

makes the obtained activated carbons economically feasible. These activated carbons from olive-waste cakes showed a high capacity to adsorb herbicides (2,4-dichlorophenoxyacetic acid, 2,4-D- and 2-methyl-4-chlorophenoxyacetic acid, MCPA) from water, with adsorption capacity values higher than those corresponding to a commercial activated carbon used for treating drinking water [20].

(c)   Example 1.8 (technology of separation of organics).   Separation of paraxylene from metaxylene and/or ethylbenzene by adsorption [21], in the technical aspect, is preceded by the process of zeolite preparation. Adsorbents like X and Y zeolites are exchanged with potassium and barium cations and associated with an adequate solvent. After this procedure, the zeolites are efficient for paraxylene separation by adsorption. Paraxylene selectivity can be observed only at high loading and for bulky and weakly charged cations. Entropy effects allow paraxylene to be more efficiently packed in the zeolite micropores. Due to this fact, the value of paraxylene–metaxylene selectivity is over 3, while paraxylene–ethylbenzene over 2, which is enough for the effective separation [21].

(d)   Example 1.9 (technology of catalytic synthesis).   This example demonstrates the synthesis of fine and intermediate chemicals on immobilized catalysts [22]. Homogeneous catalysts (e.g., homogeneous transition metal complexes supported on zeolites with mesopores completely surrounded by micropores, homogeneous transition metal complexes on mesoporous MCM-41, and ionic liquids on various carriers) can be transformed to recyclable heterogeneous catalysts. The catalysts are very effective in reactions such as oxidation, hydrogenation, and carbon–carbon bond formation [22].

(e)   Example 1.10 (technology of catalytic synthesis).   Multiuse selective catalysts–amorphous microporous mixed oxides (AMM) can be described as catalysts prepared to contain isolated catalytically active centers in the shape selective environment of micropores. The lack of inherent limitations with respect to chemical composition and pore size makes AMM materials versatile catalysts for many uses. AMM can be effectively used in such processes as hydrocracking, redox catalysis with organic hydroperoxides, redox catalysis with hydrogen peroxide, acid-catalyzed etherification and esterification reactions, oxidative dimerization of propene with air, selective oxidation of toluene to benzaldehyde with air, and selective aromatic alkylation. AMM can also work in microporous catalyst membranes [23].

(f)   Example 1.11 (technology of organic synthesis).   Catalytic versions of the Baeyer–Villiger oxidation are particularly attractive for practical

applications because catalytic transformations simplify processing conditions while minimizing reactant use as well as waste production. Corma et al. [24] evolved the Baeyer–Villiger oxidation into a versatile reaction widely used to convert ketones—readily available building blocks in organic chemistry—into more complex and valuable esters and lactones. These authors [24] expected some benefits from replacing peracids, the traditionally used oxidant, by cheaper and less polluting hydrogen peroxide. Dissolved platinum complexes and solid acids, such as zeolites or sulphonated resins, efficiently activated ketone oxidation by hydrogen peroxide. However, it was noted in Ref. 24 that these catalysts lack sufficient selectivity for the desired product if the starting material contains functional groups other than the ketone group; they perform especially poorly in the presence of carbon–carbon double bonds. It was shown in Ref. 24 that upon incorporation of 1.6 wt% tin into its framework, zeolite beta acts as an efficient and stable heterogeneous catalyst for the Baeyer–Villiger oxidation of saturated as well as unsaturated ketones by hydrogen peroxide, with the desired lactones forming more than 98% of the reaction products. This high selectivity was ascribed to the direct activation of the ketone group, whereas other catalysts first activate hydrogen peroxide, which can then interact with the ketone group as well as other functional groups [24].

(g) Example 1.12 (technology of inorganic synthesis). Classic three-phase catalytic cocurrent down-flow trickle bed reactor was compared by Medeiros et al. [25], under the same operating conditions, with a three-phase cocurrent down-flow vector named *Verlifix*. This reactor is an association of a Venturi device set above a fixed bed. The Venturi device allows a good gas–liquid mass transfer and a homogeneous distribution of the gas and liquid flow. The chemical reaction studied, in both reactors, is the catalytic oxidation of sulfur dioxide on active carbon particles. All experiments have been carried out at 25°C. It was found in Ref. 25 that the presence of a Venturi distributor increased the gas–liquid mass transfer, the wetting efficiency of the catalyst and improve the conversion of sulfur dioxide. The Verlifix reactor is particularly adapted for heterogeneous reactions limited by gas–liquid and solid–liquid mass transfer [25].

(h) Example 1.13 (specific reactions impossible in ordinary conditions and allowed due to adsorption in micropores).   Some effects such as phase change and phase growth in porous media [26] occur in micropores only due to their excess energy, such as the confinement in phase transitions in micropores, the growth and dissolution of gas and liquid phases. Applications of these effects range from capillary condensation to drying to gas evolution to condensation.

Due to higher internal energy, micropores allow the best character-istics of adsorptive processes. However, if the adsorbent is regenerated by desorption, this process is seriously hindered in micropores, and the resulting energetic efficiency of the cycle adsorption–desorption, to be compared to other separation techniques, needs numerical evaluations. On the other hand, micropores have the definite advantage in the amount of the adsorbed fluid per mass unit of the adsorbent. Microporous adsorbents are absolutely preferable if the adsorbed substance is not desorbed but decomposed or oxidized (as was considered above, the oxidation of the adsorbed organic pollutants on active carbon not only regenerates the active carbon but even increases its amount, due to the products of the oxidation).

Adsorption is realized mostly due to open pores, much less to semiopen. Closed pores do no participates in the adsorption of all. The regular structure may have a significant advantage in comparison with the random structure: pores are optimally organized and do not hinder one other in the process of adsorption. That is one of the reasons why the selective separation by zeolites is preferable.

Heterogeneous structures have several disadvantages in comparison with homogeneous structures, because of different local partial pressure (concentration) of the adsorbed substance against various parts of the heterogeneous adsorbent [27,28]. For the same reason, desorption processes are better organized on homogeneous adsorbents.

C. Percolation and Permeability

Percolation and permeability are found only in open pores. The value of permeability is larger in the case of macropores, just for geometrical reasons. However, only micropores allow the selective separation of components in fluid flows [29,30].

The fact of percolation does not depend on the regularity or the randomness of a porous structure, however, if the percolation is found, the regular structure has more permeability—again, because its pores are "optimally organized."

Heterogeneity is favorable for increasing permeability—for the same reason that heterogeneity is not favorable for the insulation.

(a) Example 1.14 (selectivity of ultramicropores and high-selectivity membranes). The selectivity of micropores and ion channels was examined for simple pore topologies within the framework of density function theory of highly confined fluids [29]. It was shown that in an infinite cylindrical pore purely steric (excluded volume) effects lead to strong, nontrivial size selectivity, which is highly sensitive to the pore radius [29].

(b)   *Example 1.15*.   In the estimation of Canan [31], vapor-phase sorption is the most influential process governing the transport and the fate of volatile organic compounds in soil. The single-pellet moment technique was used to investigate sorption and diffusion of trichloromethane (TCM) and carbon tetrachloride (CTC) at varying relative humidities (0–80%) of synthetic humic–clay complex pellets consisting of clay (montmorillonite) and different amounts of organic matter (humic acid). The effective diffusivities of TCM and CTC did not show a noticeable change with moisture and humic acid content. On the other hand, with increasing humic acid content of clay at zero relative humidity, an appreciable decrease of the equilibrium sorption constants of the tracers (TCM, CTC) was found because of the blockage of some sites of the mineral surfaces and especially micropores by the humic acid. The presence of water also reduced dramatically the sorption of TCM and CTC on synthetic humic–clay complexes. Above 20% relative humidity, the sorption coefficient of TCM and CTC varied only slightly with humic acid content. It was concluded that the sorption of TCM and CTC in synthetic humic–clay complexes was strongly effected by the moisture and humic acid content [31].

D. Mechanical Properties

For most known materials, microporosity and homogeneity are favorable for better mechanical resistance and elasticity. Opening and closing pores does not influence the mechanical characteristics. Regular materials, as in many similar situations, have better mechanical properties than randomized ones—for the reason of "optimal organization" of the structure.

The results of the analysis of the relationship between the structural characteristics and the measurable properties of porous materials are given in Table 1.8.

The structure of pores is very difficult to control; therefore, we are much more interested in the relationship between the conditions of preparation of a porous material and its measurable properties. An example of such a relationship is given by Table 1.9.

V. ENERGY DISTRIBUTION OF PORES

Above, presenting the classification of pores, we mentioned the classification by the characteristic size and noticed that micropores are characterized by the energy much better than by the size. The main reason for the micropore pore classification by size is the tradition of IUPAC but not physical considerations. In Chapters 3 through 5, presenting mathematical

TABLE 1.8 Relationship Between the Structural Characteristics and the Measurable Properties of Porous Materials

Structural factor	Insulation	Adsorption	Percolation or permeability	Selective separation	Mechanical resistance or elasticity
Size of pores	Micropores are preferable	Micropores are preferable	Macropores are preferable	Micropores required	Micropores are preferable
Opening and closing of pores	Closing is preferable	Opening required	Opening required	Opening required	Indifferent
Randomness or regularity	Randomness is preferable	Indifferent	Regularity is preferable	Regularity is desired	Regularity is preferable
Homogeneity or heterogeneity	Homogeneity is preferable	Homogeneity is preferable	Heterogeneity is preferable	Homogeneity is preferable	Homogeneity is preferable

TABLE 1.9 Conditions of Preparation of Porous Materials, Allowing the Obtainment of Several Needed Properties

Property desired	Needed regime of treatment of solid raw material[a]	Needed regime for the simultaneous synthesis of pores with the solid[a]
Insulation	Careful oxidation of organic solid	Polymerization with intense cross-linking and moderate oxidation
Adsorption	Moderate oxidation of organic solid	Thermal polymerization without cross-linking
Percolation or permeability	Deep thermal oxidation of organic solid	Moderate-degree polymerization, no cross-linking
Selective separation	Dehydration of zeolites	Special careful oxidation of organics
Mechanical resistance and elasticity	Moderate chemical oxidation of organic solid	Polymerization with careful cross-linking

[a]The table presents not all available solutions but some examples only.

models related to various aspects of microporosity, we will use not characteristic size but energy.

Energy of macropores (per internal volume unit) is very low; the energy of mesopores (per internal surface or volume unit) is moderate; the energy of micropores (per volume unit) is high or very high. In principle, the characteristic energy per volume unit could be the criterion for the classification of pores, instead the characteristic size.

However, since micropores work in assemblages, their characterization should be collective. For this aim, we use the function of *energy distribution of micropores* or *micropore distribution in energy* $F(\varepsilon)$ (more exactly, free energy by Gibbs). Here, F has the statistical sense and presents the volume fraction of micropores, energy of which is from ε to $\varepsilon + d\varepsilon$, where $d\varepsilon$ is a very small value. For statistical reasons,

$$\int F(\varepsilon) = 1 \tag{1.4}$$

where the integration is taken on all the spectrum of values of ε. The energy distribution is related to the differential enthalpy, differential entropy, and immersion enthalpy via traditional thermodynamic relationships. For

macropores and mesopores, one can find analytical relationship between energy and size distributions.

For some systems, one can evaluate $F(\varepsilon)$ from quantum considerations [32].

The energy distribution of micropores in a material can be estimated on one of the following ways:

Assumption of energy distribution

Derivation of the energy distribution from certain model considerations

Indirect estimation of the energy distribution from experimental data

Experimental methods for studies of micropores, particularly for the estimation of their energy distribution, will be considered in Chapter 2.

VI. FRACTALS IN POROUS STRUCTURES

Fractal is defined as a structure in which each fragment repeats the same configuration, and the entire structure has the same configuration (see Fig. 1.11).

Obviously, all regular fractals are regular structures. However, not all regular structures are fractals. All crystals are regular fractals.

Fractals on Fig. 1.11 have simple configurations. Of course, if the configuration is more complex, that does not change the sense of the phenomenon of fractal. One may ask whether the configuration can be random? The answer is positive. Such fractals, fragments of which randomly repeat on different scales, are defined as *random fractals*.

The first observation of random fractal was related to maps of the British coast line: its configurations in various scales were found very similar.

```
        A              BBBBBBB

        AA           BB      BB

       AAA           BB      BB

      AAAA           BBBBBBB

     AA  AA          BB      BB

   AA     AA         BB      BB

  AA       AA        BBBBBBBB
```

FIG. 1.11 Regular fractals: configurations A and B, respectively.

Random fractals correspond only to homogeneous random structures. Random fractals are observed for many known macro- and mesoporous structures. What about microporous structures? As it was mentioned above, their direct observations are impossible. Moreover, the scale of below 1 nm makes the existence of fractals theoretically impossible. However—it is much more important—*properties of homogeneous random micropororosity are well described by the random fractal approach.*

The theoretical and numerical aspects of random fractals will be analyzed in Chapters 3 and 5.

The priority of porous structures in the fractal concept is absolutely due to Benoit Mandelbrot.

In the theory of porosity, the fractal approach is largely used for modeling formation and structure of microporous media, comprising such complicated processes as microporous catalyst synthesis. One of methodological advantages of the fractal approach consists in its compatibility with most of existing theoretical methods. For example, Tsekouras and Provata [33] considered spontaneous local clustering on lattice and homogeneous initial distributions turn into clustered structures, at the surfaces of which the reactions take place, using mean-field analysis and Monte Carlo simulations [33].

The aspect of the compatibility of the fractal approach with other theoretical methods will be considered in more detail in Chapter 5.

The usefulness of the fractal approach in modeling of macromolecule separation processes in packed columns was illustrated by Ref. 34. In these columns filled with porous particles the macromolecule retention mechanism is determined by size-exclusion chromatography (SEC), hydrodynamic chromatography (HDC), or their combination [34]. It was proved that the degree to which SEC and HDC are mixed depends on the particle diameter, the relative size of the pores, and the macromolecule size. Guillaume et al. [34] showed the fractal character of the apparent selectivity between two adjacent peaks on the chromatogram.

The fractal analysis seems also effective in accounting nonhomogeneous distribution of porosity and quantifying the drag correction for flow through effects, e.g., by treating an individual aggregate as a self-similar object made up of a settling swarm of permeable spheres that are themselves made up of a settling swarm of subspheres and so on to the level of primary particles [35].

One can notify some other applications of the random fractal concept (not related to porosity):

1. *Biochemistry of proteins.* Fractal structural tendencies are found for distributions of small-angle neutron scattering (SANS) used

to study the structure of protein–sodium dodecylsulfate complexes [36]. Analyses of SANS distributions clearly showed that the arrangement of micellelike clusters resembles a fractal packing of spheres. Guo et al. [36] showed that a protein–SDS complex can be characterized by four parameters related to the fractal model and extracted from the scattering experiment (the average micelle size and its aggregation number, the fractal dimension characterizing the conformation of the micellar chains, the correlation length giving the extent of the unfolded polypeptide chains, and the numbers of micellelike clusters in the complex) [36].

2. *Biochemistry of proteins*. Liebovitch and Todorov [37] presented an analysis of opportunities related to the use of fractal concept and nonlinear dynamics in studies of ion channel proteins:

   a. Existence of long-term correlations in channel function and self-similar properties of the currents recorded through individual ion channels, characterized by a scaling function.

   b. Possibility of fractal form for the whole-cell membrane voltage recorded across many channels.

   c. The appearance of the same distributions of open and closed times for random events and the deterministic dynamics [37].

   d. Liebovitch and Todorov [37] debate whether random, fractal, or deterministic models best represent the functioning of ion channels.

3. *Theoretical biochemistry*. Aiming to describe cellular cytoplasm, Aon and Cortassa [38] suggested its analogy with a percolation cluster, a sort of "random fractal," with a quantification of the fractal dimension D in micrographs of cytoskeleton components or microtrabecular lattice. Their hypothesis dealt with

   a. The existence of the percolation threshold.

   b. The reactivity increase when enzymes (or targets) and substrates (or effectors) coexist in the same topological dimension [38].

4. *Anatomy*. Aiming to investigate the resting heart rate (HRV), Yamamoto et al. [39,40] assumed the basic fractal nature of its variability, relative to that in breathing frequency (BFV) and tidal volume (TVV), and tested the hypothesis that fractal HRV is due to the fractal BFV and/or TVV in humans. In addition, the possibility of the fractal nature of respiratory volume curves (RVC) and HRV was observed [39,40].

5. *Theoretical biophysics*. According to Ref. 41, recent mathematical analyses had shown fractal properties for some seemingly irregular

biological signals. A fractal time series was characterized by the property of self-similarity (self-affinity) and had long-range time correlation. The aim of the study [41] was to investigate the question of whether the fluctuation of H-reflex was fractal with strong time correlation. The results obtained in [41] indicated that

   a. The fractal correlation found in the H-wave sequences was caused neither by the conduction through nerve fibers nor by the transmission at the neuromuscular junction because the M-wave sequence had a significantly weaker time correlation.

   b. Special impulses in a motor nerve induced by the stimulation made a minor contribution to the generation of fractal correlation in the H-wave sequences because it was preserved when the stimulation intensity was below MT. It was suggested that the fractal correlation in human H-reflex was generated at the synaptic connections to alpha-moto-neurons in the spinal cord [41].

6. *Studies of human brain*. Mather [42] studied images of three-dimensional scenes that inevitably contain regions that are spatially blurred by differing amounts, owing to depth-of-focus limitations in the imaging apparatus. Computational modeling had shown that the effect of blur on single-step edges was very similar to its effect on random fractal patterns, because the two stimuli had similar Fourier amplitude spectra [42].

7. *General biology and pharmacology*. It was found in [43] that fractal analysis is suitable for analyzing liver fibrosis and has excellent reproducibility. Moal et al. [43] estimated fractal analysis as the only quantitative morphometric method able to discriminate among the models of fibrosis and sensitive enough to detect pharmacologically induced changes in liver fibrosis [43].

8. *Environment engineering*. Fractal approach is used also in modeling processes in multiphase (soil–atmosphere–oil–water) flow systems [44]. That allows the application of light transmission method (LTM), based on the use of the hue and intensity of light transmitted through a slab chamber to measure fluid content, since total liquid content is a function of both hue and light intensity, when comparing experiments with LTM and synchrotron x-rays. As result, the contaminant concentrations are measured, and the risk to human health and the environ-ment because of contaminating groundwater resources is minimized [44].

9. *Geophysics* (certainly, because that was the beginning of the random fractal concept). Numerous natural network systems have fractal structures that are optimal for minimizing energy expenditure during material transport. It was shown in Ref. 45 that a fractal magma ''tree'' provides a network in which magma rapidly loses diffusive chemical ''contact'' with its host matrix.

VII. CLASSIFICATIONS OF MODELS OF POROSITY

As it was noted above, interactions in micropores pores and around them have quantum origin. Therefore, for the correct description of microporous structures, one should solve the Schroedinger equation for the entire solid system— which is absolutely impossible. In the real practice, one uses several assumptions based on the general physical comprehension of porosity. According to the kind of such assumptions, the existing models of porosity can be classified according to their

Applicability to such or such aspects of porosity (pore formation, characteristics of structure, measurable properties, or their combinations)

Determinism or randomness

Continuousness or discreteness

Limited or unlimited number of counted elements of the porous structure

Analytical or numerical method of simulations

Level of assumptions (fundamental physical, just for this model, empirical treatment of experimental data)

Let us note that some models are intermediate and partly satisfy both criteria in several classification.

Of course, in the methodological aspect the fundamentally based models have a preference, but we know some situations when models were formulated initially based on experimental results or intuitive assumptions and later received fundamental support. For example, Dubinin's assumption of Gauss energy distribution got explanation in Ref. 11 as sequence of casual (Monte Carlo) approach. Fractal model suggested by B. Mandelbrot was due to observations and empirical suggestions presented in Ref. 11, a thermodynamic explanation.

In Table 1.10 we present some examples of existing models of porosity based on fundamental physical assumptions in the light of the above classifications.

TABLE 1.10 Classification of Some Existing Models of Porosity

Model	Application	Determinist or random	Continuous or discrete	Limited or unlimited counting	Analytical or numerical
Monte Carlo	All aspects	Random	Discrete	Limited	Numerical
Gauss energy distribution	Structure only	Random	Continuous	Unlimited	Analytical
Gauss size distribution	Structure only	Random	Continuous	Unlimited	Analytical
Gibbs energy distribution	Structure only	Random	Continuous	Unlimited	Analytical
Chemical model	Preparation and structure	Randomness with elements of determinism	Discrete	Unlimited	Analytical
Statistical polymer	All aspects	Randomness with elements of determinism	Discrete	Limited	Numerical
Monte Carlo with thermodynamic limitations	All aspects	Randomness with elements of determinism	Discrete	Limited	Numerical

The detailed analysis of existing models of microporous structures, with discussing numerical results, will be presented in Chapter 5.

VIII. CONCLUSIONS

1. Porous structures can be classified in accordance to the following features:
   a. Pore size or energy distribution
   b. Fractions of open, semiopen, and closed pores
   c. Regularity or randomness
   d. Homogeneity or heterogeneity
      Micropores are better characterized by energy than size.
2. All characteristics of porous structures are determined by the technology of their preparation and determine all measurable properties of porous materials. Processes of formation of micropores, mesopores, and macropores compete, and their rates depend on both the kind of raw material and the technology of its treatment. Microporous substructures are formed due to chemical reactions in the condensed phase and determine such specific properties of porous materials as heat or mass transfer, adsorption, percolation or permeability, and mechanical resistance.
3. Models of porosity can be classified in accordance to the following characteristics:
   a. Applicability to aspects of porosity (pore formation, characteristics of structure, measurable properties, or their combinations)
   b. Determinism or randomness
   c. Continuousness or discreteness
   d. Limited or unlimited number of counted elements of the porous structure
   e. Analytical or numerical method of simulations
   f. Level of assumptions (fundamental physical, just for this model, empirical treatment of experimental data)
      Theoretical modeling of microporosity is especially important for research of porous materials because the experimental information about them is indirect and characterized by significant error of measurement.
4. Though the fractal concept of porosity exists due to observations of large pores, the fractal approach is especially important for the description of micropores, because of technical difficulties related to the measurement of their properties.

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