

Microstructure and Thermal Analysis of Solid Surfaces

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Preface

Until some years ago it was assumed that the investigation of the fine structure of surfaces is only necessary in particular fields of technological research and production control, e.g. in the manufacture of adsorbents and catalysts. Today it is realized that characterization of the surface and pore structure is advantageous whenever quantitative data are required for reactions at the surface of a solid. This applies to physical reactions, such as adsorption or absorption, dissolution, and crystallization; to electrochemical reactions at electrodes; and to chemical reactions in which the solid is converted, e.g. corrosion. The experimental methods described in this book are furthermore of importance in the increasing application of fine porous materials in technical processes as carriers for catalysts, adsorbents and matrix material for the storage of substances.

The surface of a solid differs from the bulk basically by two features:

- the surface has an open geometric structure, and the arrangement of the atoms differs from that in the bulk
- the surface atoms are bound only unilaterally, and they have free valences ready to bind foreign atoms of the adjoining phase.

These facts have to be regarded in all processes where solid phase boundaries are present because the course and kinetics of reactions can be strongly influenced by the surface properties. With regard to the miniaturization of all devices in mechanics, electronics, optics, etc., the surface in comparison to the bulk is increased and thus surface effects like corrosion, adhesion, and surface charge gain increased importance.

The book covers the basic methods of investigating the surface with respect to its geometry, its chemistry, and its treatment by heat. Research on surface reactions and processes occurring or starting at the surface of a solid, like sorption, heterogeneous catalysis, friction, lubrication and glueing, degassing, drying, corrosion, and surface treatment, requires knowledge of some of the following parameters: surface geometry, pore structure, particle size distribution; specific surface area; chemical composition of the surface; valency spectrum; composition of adsorbed layers; and electronic work function.

The book also presents methods of surface analysis, especially based on experiments with gases and liquids in contact with the surface investigated; it touches upon microscopy and scattering experiments with light, electrons, and ions. Measurement of electric properties and valences, however, was not considered to be appropriate.

Part 1 deals with the investigation of the geometric properties of the surface, Part 2 with that of the chemical surface properties, and Part 3 describes in some detail the gravimetric techniques widely used by the authors, and some useful appendixes complete the work.

The treatise is based on many years' experience gained in experimental work at the Laboratory of Surface Chemistry, Ain-Shams University, Abbassia-Cairo, and the Interfaces Research Section, Battelle-Institut e.V., Frankfurt am Main.

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Part 1

Geometry of Solid Surfaces

Introduction to Part 1

When examining a surface visually, even by means of the light microscope, only structures above $0.1\ \mu\text{m}$ can be observed. Thus an optically smooth surface can reveal a highly rugged structure. Inspecting a well-machined piece of material we have to take into account:

- deviations from the ideal shape
- surface roughness
- internal pore structure, where we have to distinguish between open pores accessible for molecules of the surrounding atmosphere and closed pores accessible only by bulk diffusion.

A diagram of a well-machined metal surface is shown in Fig. 1 depicting:

- (a) the shape deviation as seen with the aid of an optical instrument
- (b) the surface roughness which can be detected by e.g. tactile response to a diamond pin; and
- (c) the surface pore structure revealed by an electron microscope.

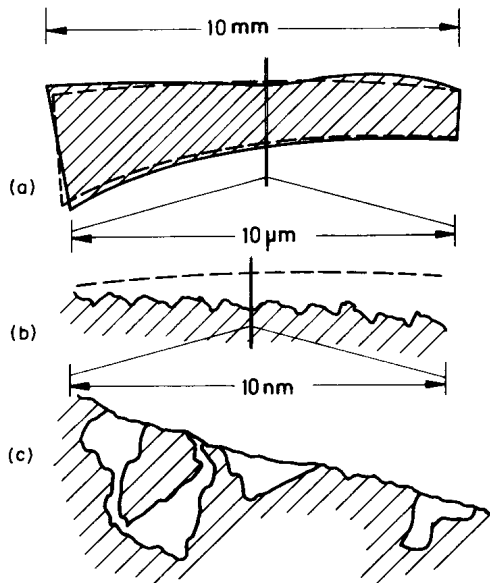


Fig. 1 Diagram of a section through a metal piece normal to the well-machined surface under increasing magnifications: (a) deviation from desired shape; (b) surface roughness; (c) micro- and mesopore structure

Many catalysts, adsorbents, and many powders dispose on surface areas of some hundred square metres per cubic centimetre, or $10^8 \text{ m}^2/\text{m}^3$. This surface area is situated mostly inside the grains, pellets, etc. Thus the visual boundary layer hides an internal surface area which is at least 1.05 up to 10^6 times larger than the geometric projection area.

The first part of this book covers the investigation of the geometry mainly in the sub-micron and nanometer range. Shape deviations, roughness and grain size determination will be dealt with briefly because these parameters can be measured just as well with methods for the analysis of the sub-micro-geometric range.

The complexity involved in the analysis of solid surfaces, especially amorphous solids, lies in the difficulty of obtaining reproducible properties of various samples of the same material. This complexity is due to several facts. Firstly, high surface area solids are formed, in the majority of instances, by polymerization processes; heterogeneity is created due to irregular packing of macromolecules as well as to incompleteness of the condensation reaction between these macromolecules. Therefore, the geometry and chemical composition of the surface depends to a large extent on the method used in obtaining these inorganic or organic polymers in a certain medium, which affects their structure. Secondly, removal of the liquid phase subsequent to preparation, and for oxides, dehydration and dehydroxylation of the bulk and the surface of the solid, are complex and irreversible processes, but the extent to which these processes take place is the factor which determines the property of solids in specific molecular interaction. Thirdly, the solids, during their synthesis and subsequent treatment, capture all the possible accompanying elements and impurities; these impurities drastically affect the chemical characteristics of the resulting solid surface.

Consequently, analysis of solid surfaces should involve analysis of both the physical characteristics (geometry) of the surface, namely the specific surface area and the pore structure, as well as the chemical composition of the surface. The last decade has witnessed the transition from surface chemistry as a branch of physical chemistry dealing mainly with capillary phenomena, to the chemistry and physics of the solid surface itself, i.e., to the study of the dependence of the properties on the extent, location, and chemical composition of solid surfaces, by use of modern methods: structural, chemical, spectral, mass-spectral, isotopic exchange, catalytic, calorimetric, etc. Various *modus operandi* must be applied to the same sample under comparable conditions^{1,2}.

The vast majority of practical solids are porous. Indeed, production in the laboratory of solids that are sufficiently nonporous that their internal surface and void structure can be ignored is somewhat problematical. When a solid is prepared from a parent material, e.g. by thermal treatment, the final solid is very often porous even if the parent material was nonporous. Moreover, in most cases, the pore structure either suffers from a tendency toward spontaneous irreversible changes, or is susceptible to changes caused by external

variables. For the minority of solids which are nonporous, it is the chemical composition of their surfaces, beside their surface extent, which determine their surface character. For the majority of solids which are porous, the size, shape, and distribution of pores play an extremely important role, which adds a third important factor, beside the chemical composition and the extent of the surface in determining their surface character. Obviously, the first step in physical analysis of solid surfaces should involve the detection of porosity before proceeding to the actual characterization of the surface in terms of surface area determination and pore structure analysis by different methods.

Four chapters are included in this part of the book; these are:

Chapter 1: The origin of pores, and the classification of porous solids

Chapter 2: Detection of porosity in solids

Chapter 3: Methods of surface area determination

Chapter 4: Methods of pore structure analysis.

Chapter 1 will serve mainly as an introduction which will be helpful for an investigator in making a choice among alternatives for the interpretation of data. Chapter 2 is demanding, because all fundamental concepts, definitions, and methods of analysis of surface area and pore structure (Chapters 3 and 4) will mostly depend on a precharacterization of the solid, and orienting its surface character in between two extreme cases, namely nonporous or totally microporous. It is not an understatement to say that the methods to be discussed in Chapters 3 and 4 should clarify the discussion of the two extreme cases, and that for an actual solid of intermediate character, the investigator should apply the method which gives a minimum margin of error, based on the actual pore structure of the solid.

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Chapter 1

The Origin of Pores, and the Classification of Porous Solids*

The analysis and classification of pore sizes, and size distributions, irrespective of their origin, has been a subject of great interest to many authors¹. We feel, however, that it is of value to include considerations of origin in the classification scheme. This is because the methods by which pore distribution is determined are strongly dependent on certain geometric features of the pores themselves, and knowledge of the origin of pores allows an investigator to make a choice among alternatives for the interpretation of his data.

We will adopt the terminology suggested by IUPAC in 1971². The narrowest pores, of width not exceeding about 2 nm, are called micropores; the widest pores, of width exceeding about 50 nm, are called macropores; and the pores of intermediate width are termed mesopores.

The origin and the stability of the pore structure of solids are extremely important, especially with regard to:

- (a) the control of pore structure, e.g. the need for tailoring the pore structure to suit particular applications;
- (b) the control of the conditions which cause metamorphic changes that modify the structure during preparation or afterwards, e.g. in storage and in practical use; and
- (c) to serve as a guide in considering a particular pore model needed for pore structure analysis in the absence of direct observation of pore shape.

Several authors³⁻⁶ have tried to develop a classification system for pores based in a major way upon their origin, and as a preliminary it should be noted that in essentially every practical porous system, the structure might exhibit more than one of the features that are described separately below. We will return to this question of complexity later on.

1.1 Pores in compacted powders

The simplest case to deal with is a system composed of spherical, nonporous particles, which, on compaction, generates a well developed, more or less uniform pore structure in which the pore space is made up of the interstitial voids between the particles. The pore volume will depend on the particle size and the average coordination number.

*Based largely on Ref. (6)

We will not go into detail here regarding the ideal packing of *uniform* spheres, for two reasons. First, a great many textbooks and treatises on physical metallurgy, X-ray crystallography, and crystal chemistry discuss this subject at considerable length. Second, the ideal packing is very seldom realized in practical bodies formed from powders or grains. There are three reasons for this non-ideality: (1) The grains are seldom of uniform size or shape, let alone spheres. (2) The average coordination number is rarely that of a close-packed solid, i.e. 12 for hexagonal close packed (HCP) and face centered cubic (FCC) lattices except for very local regions of the aggregate; local regions of coordination number 8 (corresponding to a body centered cubic (BCC) lattice) or lower are, in general, randomly intermixed. (3) The structures of such a system are commonly very seriously modified by the temperature and applied pressure to which the material is subjected.

The first two reasons for nonideality require little comment at this point; but the third has some manifestations that were not completely predictable before experimental studies were made. We will discuss the effects of temperature first.

With an increase in temperature, sintering commences. According to the classical work on metal powders, three stages of sintering can be distinguished.

1. Elimination of internal porosity of the discrete particles. This has been referred to as 'smoothing'¹; this stage does not, however, include changes in the external topography of the particles. It probably occurs largely by a surface diffusion mechanism, particularly with regard to the elimination of internal micropores in primary particles.
2. Adhesion. Discrete particles, which at low temperature constitute a loose powder, develop points of contact that have sufficient mechanical strength that the powder is converted into an aggregate that has a little mechanical strength. This stage occurs near the Tammann temperature, which is approximately half the absolute melting point. There is some surface transport in this stage (though little loss of surface area) and bridging between particles, by curved-neck connections, commences. The solid mass contains macro- and mesopores, at this stage. If surface transport is extensive, closed-off pores may develop, which are not connected to the exterior surface.
3. Shrinkage. Further heating causes onset of the third stage, during which pore shrinkage occurs, with fastening of the bridges between particles; and 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.

The classical mechanism of sintering, outlined above, does not seem to hold for certain very fine particles. It has been demonstrated by Teichner and

co-workers⁷ that, in the case of TiO_2 particles of diameter 100 nm or less, the contact between two adjacent particles does not form a curved neck. The initial step is for spheroidal particles to become polyhedral. Adhesion then occurs between the flat surfaces of the neighbouring particles. It is to be expected that this behaviour will be present with solids for which the surface energy of faces other than one or two low-index planes is much higher than that of the low-index planes.

Compaction pressure, which is the second external variable for this group of solids, leads to a decrease in the pore volume and, in most (but not all) cases, a diminution in surface area as well. Mica constitutes a clear example of a decrease in surface area under compaction. This decrease is attributed to the fact that the particles are flaky, with an extensive area of very flat surface, which is eliminated when particles adhere to each other.

The effect of pressure has been found to depend 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 coal⁸. With sucrose, the fragments move to occupy the available space, while with coal, there is tendency for fragments to remain wedged, in the form of bridges, which help to preserve an open structure. There is, as might be expected, only a modest change (decrease) in surface area when hydrostatic pressure causes particle fracture as well as compaction. It is sometimes found that when pressure has caused fracture, higher temperatures are required to produce significant sintering than when pressure has not been applied.

As already noted, the particles from which a porous solid are formed are rarely spheres; and they are seldom of equal size, whatever their shape. Even when they are relatively uniform and nearly spherical, they are seldom in close-packed arrays. The mean coordination number for random particle-packing is, in general, less than the closest-packed value, 12; and it may be lower than the BCC value, 8. If the particles are all of equal size, the more irregular the particles, the lower the mean coordination number will be, and the larger and more irregular the voids. Initial nonuniformity of voids will (to a considerable extent) persist in sintered or otherwise consolidated bodies.

In the far more common case of unequal particle size, the void volume is frequently (but not always) reduced below the volume fraction of voids in beds of uniform particles. The pore structure becomes correspondingly more complex in such systems.

1.2 Pores in gels

1.2.1 *Precipitated gels*

Metal hydroxide or hydrous oxide gels and precipitates, formed from solution, can be obtained in a wide range of pore structures. Once the gel is formed from solution, it starts ageing, i.e. it undergoes irreversible structural and

textural changes, which continue during and after the removal of the liquid phase. Three distinct stages have been described⁹ for the ageing of flocculated, hydrous gels. There are no sharp demarcations separating them; and any two consecutive steps can overlap with each other.

The three ageing stages are: (a) condensation polymerization, (b) aggregation-cementation, and (c) crystal growth and recrystallization. Stage (a) is often accompanied by the development of a large surface area and the creation of uniform microporosity. Stage (b) involves the loss of area, often with concomitant loss of micropores and development of mesopores. Stage (c), which is a slow process unless accelerated by heat, can lead 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 the three processes can take place. In certain cases, elimination of the liquid phase can by itself lead to unusual but characteristic pore structures. A well-known example is the aerogel structure, which is an open gel system with a large pore volume. The particles that make up the solid phase have a small average coordination number, typically between 2 and 2.5. Such a system 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 and an increase in average coordination number to something in the range of 6.

Precipitation of insoluble compounds other than hydroxides can lead to gels; but the steps following primary precipitation are commonly much simpler than those with metal hydroxides. Usually, such steps consist principally of crystal growth, with disappearance of the smaller and more imperfect crystals. Porous solids prepared from such precipitates commonly have pore morphologies resembling those obtained with a compacted powder (see section 1.1), unlike the gels obtained from metal hydroxides.

1.2.2 Topochemical and through-solution gels

In some cases, a primary solid is capable of further chemical interaction with water, leading to the formation of a gel, either by a topochemical or through-solution mechanism. The gel is precipitated in the water-filled spaces of the primary structure; and it can undergo a subsequent change of composition, and shrinkage, leading to a characteristic micropore structure. Typical examples are Portland cement and other types of cements, as well as gypsum. The following discussion is based on the theory of cement hydration and aging proposed by Powers¹⁰.

When dry cement is mixed with a limited volume of water, it forms a cement paste. Extensive studies of cement paste have led to the conclusion that it exists, initially, as a conglomerate of relatively discrete particles of the unhydrated cement grains and calcium sulphate. In the presence of water, this

develops into a conglomerate of (1) 'cement gel'; (2) calcium hydroxide and small amounts of other coarsely crystalline hydration products; (3) residual unhydrated cement grains and portions of grains; and (4) 'capillary pores', which are in the macropore and mesopore ranges. These are the remnants of water-filled void space that had existed between the cement grains at the time of the start of setting.

The most important of these constituents is thought to be the cement gel, which has an unusual structure. It is viewed as consisting of a solid part, the finely divided or colloidal hydration products, which are mostly calcium silicate hydrate; and a non-solid part, the 'gel pores'. The pores are treated as an intrinsic part of the gel. The gel pores are initially filled with water, but the water can be removed by evaporation, as can the water in the capillary pores. The average size of the gel pores may be interpreted in terms of the hydraulic radius, and estimates of hydraulic radii of the order of 0.75 nm have been cited¹⁰. This value implies an average distance from surface to surface of 1.5 to 3 nm, depending on the pore shape.

In contrast to the characteristic volume and size of the gel pores, the capillary pore constituent of the paste is thought to vary in volume (and perhaps in void size), depending mainly on the water/cement ratio and the degree of hydration of the particular paste. An interesting conclusion has also been reached¹⁰ that in pastes of water/cement ratio less than about 0.38 that have been allowed to hydrate continuously, all the capillary voids eventually become filled with gel. Quantitative evaluation of the size ranges to be ascribed to capillary pores are virtually nonexistent. Nevertheless, it is maintained that those are generally order of magnitude larger than gel pores.

Finally, it is believed that the capillary pores constitute an interconnected, continuous network in fresh cement paste; but for pastes of normal water/cement ratio ('normal' meaning ratios between 0.4 and 0.7) it is considered that the capillary 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. Thus, in this kind of material, additional hydration offsets ageing effects.

The pore structure of this group of solids is particularly important because of its direct effect on the mechanical and other engineering properties of the pastes.

1.3 Pores in stable crystals

The well-known zeolites and 'molecular sieves' are examples of this group of solids, in which an intracrystalline micropore structure is distributed as channels, slits, or cavities within the lattice. The dimensions and patterns of these micropores are regular. In zeolites, the cavities are interconnected by 'windows' of diameter 0.4 or 1 nm. Zeolites and molecular sieves can be used, by virtue of their stability towards heat treatment, for trapping otherwise inert gas molecules. At high temperatures and pressures, small molecules can pene-