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SUBCOMMITTEE ON CATALYST CHARACTERIZATION†

MANUAL ON CATALYST CHARACTERIZATION

(Recommendations 1991)

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Manual on catalyst characterization (Recommendations 1991)

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1. INTRODUCTION

This manual has been prepared by the Commission on Colloid and Surface Chemistry including Catalysis of the IUPAC. It results from the general feeling among surface and catalysis chemists both from academia and industry that the rapid increase of knowledge in science of catalysis and the better understanding of the mechanism of catalytic processes is not accompanied by the development of the appropriate scientific language. Many terms, widely used in the literature, remain vague and undefined. Thus, the Subcommittee on Catalysis was created with the task of preparing a catalyst characterization chart, listing all parameters which should be specified in order to obtain a full description of a catalyst, and of formulating the definitions of these parameters as well as recommendations concerning the terminology.

The present manual is based on the same general principles as those used in the Manual of Symbols and Terminology for Physicochemical Quantities and Units of the Commission on Symbols, Terminology and Units of the Division of Physical Chemistry, Definitions, Terminology and Symbols in Colloid and Surface Chemistry of the Commission on Colloid and Surface Chemistry, Appendix II Part I Definitions, Terminology and Symbols in Colloid and Surface Chemistry, Part II Heterogeneous Catalysis, and Recommendations in Reporting Physisorption Data for Gas/Solid Systems. (ref. 1-3)

Since the present proposals should be considered as one of the sub-sets of the terms and symbols of physical chemistry, the general principles are not repeated here. (see Note a)

This manual provides definitions and recommendations concerning the terminology of catalysis. It should be read in conjunction with the Manual of Methods and Procedures for Catalyst Characterization which provides details and recommendations concerning the experimental methods used in catalysis.

2. CATALYST FORMULATION AND METHODS OF ITS PREPARATION

2.1 Methods of preparation

Many catalysts consist of an active component or components (see 2.2) deposited on a support (such as silica, alumina, carbon). The role of the support may be to improve the properties (e.g. stability) of the active component(s), or to participate directly in the catalytic reaction (e.g. by providing acidic sites). The following terms define general preparation methods.

2.1.1 Precipitation

Precipitation is a method often used for producing both support precursors and catalyst precursors (including precursory forms of zeolites) and occurs when two or more solutions are mixed in a suitable way. In addition to providing general details of the method (e.g., concentration, temperature, pH, etc.) it is necessary to indicate specifically the order and rate of addition of one solution into the other, a description of the mixing procedure and the details of the ageing procedure, if any. The association of two or more active elements in the precipitate, in a single or several phases, may be achieved by co-precipitation.

2.1.2 Deposition

Deposition describes the application of the catalytic component (e.g. nickel, as nickel nitrate) on to a separately produced support (e.g. silica). Any treatment of the support before the deposition step must be described precisely.

Deposition may be achieved by impregnation, i.e., contacting the support for a specified time with a solution containing the active elements. When the active elements are contained in a volume of solution corresponding to the pore volume, the procedure is called dry or pore volume impregnation. The term incipient wetness method is used to describe impregnation when the volume of the solution is empirically determined as corresponding to that beyond which the catalyst begins to look wet. One or several parallel processes such as adsorption, ion exchange, selective reaction on or with the surface of the support may take place during impregnation. Sometimes the

Note a: Revised and extended edition of the aforementioned 'Manual' has been published as a book under the title *Quantities, Units and Symbols in Physical Chemistry* (Blackwell Scientific Publications, Oxford, 1988).

process of impregnation is carried out by percolation of the impregnating solution through a bed of support, or by dipping the support in the impregnation solution.

Two or more active elements may be introduced either in a single step by co-impregnation or subsequently one after the other in successive impregnations. Drying and often calcination (see 2.1.5) take place between impregnations. Deposition involving the formation of a strong (e.g. a covalent) bond between the support and the active element is usually described as grafting or anchoring. This is achieved through a chemical reaction between functional groups (e.g. hydroxyl groups) on the surface of the support and an appropriately selected inorganic, or organometallic compound of the active element. When deposition takes place by adsorption or reaction from the gas phase, the term chemical vapour deposition is used.

Sometimes a special technique of precipitation-deposition is used, in which an active element (e.g. nickel) is deposited onto a carrier (e.g. silica) in suspension in the precipitating solution (e.g. nickel nitrate) by slow addition, or in situ formation (e.g. of OH^- by hydrolysis of urea) of a precipitating agent.

Ion exchange, which as already mentioned may occur during impregnation, is an important process in the synthesis of zeolites and also in the preparation of some supported metal catalysts.

2.1.3 Encapsulation

Enzymes or cells, which are of relatively large size may be entrapped in a maze of polymeric molecules (a gel). This procedure is called immobilization by inclusion. When the biocatalyst is enclosed inside a semipermeable membrane, usually approximately spherical, the method is known as encapsulation. In the process of reticulation the primary biocatalyst particles (individual enzyme molecules, cofactors or individual cells) are covalently attached to each other by organic chains, into a three-dimensional network. The term grafting is also used in this context. Attachment to the support by adsorption forces is called immobilization by adsorption.

2.1.4 Selective removal

Preparation of the catalyst by the reaction of a precursor (e.g. NiAl alloy) with a reactant (e.g. an aqueous NaOH solution) which selectively dissolves part of the precursor (Al) leaving the active agent (Ni) is described as selective removal method.

2.1.5 Treatment of intermediate solids or precursors

Very often the intermediate solid is left for some time under specified conditions in the presence of the impregnating or precipitating mixture. This is called ageing. Washing of the intermediate solids formed by precipitation is generally required to remove adsorbed ions such as Na^+ which were introduced during the precipitation.

The solvent may be eliminated without chemical transformation by drying. Many different processes may be applied to this end such as drying in an oven, fluidized bed drying, spray drying, freeze drying.

The intermediate solids are usually subjected to heat treatment, sometimes called calcination. The term calcination should only be used when heating is carried out in air or oxygen. It is essential to describe the exact conditions of heat treatment, in particular the condition of the introduction of the sample, temperature and the rate of its change, pressure, gas flow conditions, etc. Chemical transformation of the solid may take place in the course of the heat treatment. When this transformation proceeds without interaction with the atmosphere the term thermal decomposition may be used.

2.1.6 Activation of the precursor

The final step in the preparation of a catalyst is the transformation of the precursor to the active phase (e.g. metal, sulfide) which is sometimes called activation. The activation may be a reduction (e.g. by H_2), reduction-sulfidation (e.g. by $\text{H}_2 + \text{H}_2\text{S}$), dehydroxylation (e.g. by removal of H_2O from zeolite) or oxidation (e.g. by O_2). The details of the activation

process must be stated (e.g. partial pressure and purity of gas, method of heating and its rate, gas reacting flow rate, sample size).

2.2 Chemical composition

Catalytic materials are frequently composed of many components and phases. Therefore, it is seldom adequate to define a catalyst by merely stating the chemical composition, e.g. 1% Pt, 99% SiO₂. Note that by convention the support should be indicated clearly by using an oblique stroke (solidus), e.g. 1% Pt/SiO₂.

The term major active component may be used to describe the active component, the proportion of which greatly exceeds that of the others. Secondary components added on purpose may be described as additives, whereas the term impurities should be reserved for trace amounts of other elements, over which the investigator (manufacturer) has little control. The use of the word promoter implies that the additive improves some particular property of the catalysts, and it is desirable to indicate this property when known (e.g. activity, selectivity, textural properties, resistance to sintering). The term modifier is used sometimes in this context, but is not recommended. The term modifier is used in a special and proper sense in the context of asymmetric hydrogenation when, for example, Raney nickel is modified by optically active tartaric acid in order to impart the property of asymmetry to hydrogenation reactions over the catalyst.

The action of adding a small amount of foreign atoms to form a solid solution in the lattice of a nonmetallic catalyst is sometimes called doping.

The description of the composition of a catalytic system should indicate the crystallographic form of the support (e.g. γ -Al₂O₃, TiO₂ - anatase). The chemical composition should be unambiguously defined. When specifying the proportions of the active phase to the support, weights may be used provided the stoichiometry is clearly indicated (e.g. Co₃O₄ and MoO₃, Co₉S₈ and MoS₂, NiO, Pt).

2.3 Aggregate morphology

The solid obtained after the operations described in Section 2.1 (supports, intermediate solids, precursors or catalysts) can be used as such (e.g. powders) or shaped into larger entities (beads, pellets, extrudates, rings). In special cases structures called monoliths are used as support. Description of the aggregate morphology should include reference to the crystal structure and details of the shape of the particles of the various phases present, their arrangement in space (including the voids or pores) and the shape of larger physically separate entities. The structure is defined by the distribution in space of the atoms or ions in the material part of the catalyst, the texture is defined by the detailed geometry of the void space in the particles of catalyst and by the spatial relationships between the different phases present.

Certain materials used as catalysts or supports consist of spheroids smaller than 10 nm in diameter, cemented into larger entities. A primary particle should be defined as the smallest discrete identifiable entity and the method of identification should be mentioned (e.g. transmission electron microscopy, scanning electron microscopy). An assemblage of such primary particles exhibiting an identifiable collective behaviour (e.g. chemical nature of the aggregated primary particles, texture of the aggregate, resistance to mechanical separation upon grinding) constitutes an aggregate. When describing the aggregates the criterion of identification should be mentioned. Strongly bonded aggregates are called agglomerates.

A collection of loose, unattached, primary particles or aggregates of relatively small size is usually called a powder. It is recommended that the word powder is used if the largest dimension of the individual entities is smaller than 1 mm. The shape of the particle should be described (sphere, flake) and the method of its preparation specified (crushing, grinding spray drying).

In the designation of larger aggregates two criteria may be used: shape, referring to geometrical definition, or method of preparation. Spherical, spheroidal or rounded aggregates obtained by beading or granulation are called beads, and aggregates of cylindrical shape, formed by tableting

(tablet) or extruding (extrudate) are described as cylinders. The term lump is used to describe an aggregate of irregular shape, obtained usually by crushing, but its form should be described as precisely as possible. A precise description should be given when aggregates of other form, such as rings or trilobes, are used. The dimensions (diameter, thickness, length, inner and outer diameter of a ring) of the entity as defined above should be stated.

2.4 Forming operations

Depending upon the technology (e.g. fluidization, moving-bed or fixed-bed) and the conditions of the catalytic process, the shape and size of catalyst entities may vary appreciably, e.g. powder, cylinders, beads. A general problem is to make entities of dimensions larger than 1 mm from fine powder particles or precipitates. Materials which are difficult to shape are treated with additives (e.g. flake graphite, starch, stearic acid, poly(acrylic acid), mineral oil, vegetable oil) usually in amounts of 1-5wt.-%. Shaping additives may act as lubricants, plasticizers, cements, porosity promoters (porogenic additives). The powdered starting material mixed with the additives may be dry, or converted to a plastic pulp by addition of a suitable liquid.

One sometimes distinguishes:

- paste processing: grinding, kneading to a pulp, extruding;
- liquid processing: gelification (oil drop), spray drying;
- powder (or solid) processing: tableting, cementing.

If the material is of natural origin (natural molecular sieve, pumice) the desired entity size is obtained by crushing and/or grinding and subsequent size selection by sieving. Some catalysts are also obtained in this way from synthetically prepared bulky masses (e.g. ammonia catalyst). Grinding may take place in the absence (dry grinding) or presence (wet grinding) of a liquid, usually water.

In spray-drying a solution or a slurry of the powder in suspension in water is passed through a nozzle which sprays small droplets into hot air. Spray-drying gives particles of almost identical shapes (spheres with a small characteristic depression) and size which are used as such in fluid bed operations. The dropping-in-oil method consists in introducing a sol or gel as drops through a nozzle into a hot oil. Water from sol or gel is evaporated (chemical bonds may be formed at this stage) and the gel hardens, resulting in the formation of beads. Depending on the relative densities the drops may move downwards (oil drop per se) or upwards. Granulation is a process of aggregation by progressive humidifying in a rotating granulator. Generally, aggregates of different size are kept in motion under a spray of liquid (water or aqueous solution) in a horizontal rotating cylinder or a pan rotating around an axis inclined about 45°. The pan may be concave (hemispheric granulator or 'bow granulator') or cylindrical (flat granulator or 'dish granulator'). Spheroidal particles or granules are thus formed. In the method of tableting, the powder is firmly compressed in a die to be shaped into small cylinders (pellets), rings or beads. In most cases some plasticizing agents are added to the powder (talc, graphite, stearic acid). Another technique of shaping larger entities from a powder is extrusion, in which a paste is forced through a die to form a cylinder which is cut into small pieces. The cross-section of the die may have different shapes (circular, trilobe, toothed wheel, ring). The powder with the additives is first pulped with a liquid, homogenized, kneaded and fed to the die by some pushing device (screw, piston). The paste may be soft or stiff. The product is termed the extrudate, of which the exact form (see above) as well as the dimensions should be specified.

2.5 Stability of catalyst systems

2.5.1 Physical stability

Granular catalysts have a grain size distribution which may be determined by passing a sample through a series of graded sieves. The grain size distribution is determined by the condition under which the materials were precipitated or dried during catalyst preparation. Grains may be structurally weak so that they undergo attrition (see section 3.4) when in random contact with other grains. Thus grain size distribution of a catalyst may change as it is transported before use, or while it is in use. Fragmentation of catalyst particles in the reactor, caused, for example, by thermal shock or carbon build-up, may also occur.

To obtain a correct grain size distribution for a catalyst, a proper sampling procedure should be adopted. For example, samples should be taken from various depths within a container in order to determine whether the batch has been rendered inhomogeneous by settling effects, and care must be taken to ensure that the sieving process itself does not cause attrition. In the case of tableted or extruded catalysts the process of attrition may be inhibited by binders used in their preparation.

Catalysts consisting of an active phase on an oxidic or carbon support are subject to a particular form of degradation in that attrition may result in preferential loss of the active phase as fines.

Catalysts which have the capacity to adsorb water or carbon dioxide from the air may exhibit weight instability due to climatic changes. Time and variation of temperature or pressure may, in principle, give rise to losses or gains in weight due to changes in water content. Metal particles are susceptible to sintering with a concomitant loss of dispersion.

2.5.2 Chemical stability

Most heterogeneous catalysts in the as-received state or in precursor form possess a considerable degree of chemical stability whereas after activation they are highly reactive. Two cases may be distinguished: (i) chemical stability in air at ambient temperature and pressure, and (ii) chemical stability at elevated temperatures of the catalyst in the as-received state.

Many oxides, sulfides, and metals react with air slowly at ambient temperature, although such processes may be measurable only over long periods. For example, supported nickel which has been passivated by exposure to air under conditions which produce only surface oxidation may react further to give supported bulk nickel oxide. Air contains water vapour and carbon dioxide and also hydrocarbon impurities so that hydroxide or carbonate formation and hydrocarbon contamination may occur. Catalysts consisting of an active phase supported on a non-stoichiometric compound may undergo chemical change by reaction of the support with oxygen of the air. Catalysts which contain a material that is photosensitive, e.g. titania, may show enhanced chemical instability when exposed to sunlight.

Catalysts subjected to heating in air may exhibit accelerated hydroxide or carbonate formation, before a loss of water or carbon dioxide could take place. Phase changes may also occur, for example, in alumina by interaction of a partially hydrated phase with water physically adsorbed in pores. Elevated temperature may lead to measurable chemical reaction, between active phases, or between active phases and supports, or to the segregation of phases in systems that were formerly homogeneous, which greatly modify the properties of the catalyst when activated. For example, nickel oxide and silica may form nickel silicate, or cobalt oxide and alumina may form cobalt aluminate. In a nickel/silica hydrogenation catalyst, silicate formation would reduce the amount of nickel formed under standard reduction conditions. In a $\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$ hydrodesulfurization catalyst, cobalt aluminate formation would reduce the quantity of cobalt available to act as a promoter.

The nickel catalyst used in the hydrogenation of natural oils and edible fats is a special example of a catalyst which is transported in a protected state. In this case, the catalyst is protected by encapsulation in solid fat. The fat melts when the catalyst is introduced into the reactor, so releasing the active phase. Particular care must be taken to control the temperature during the transport and handling of this material.

The action of steam may have a deleterious effect on catalytic materials, For example, transport of silica can lead to loss of support material or to the encapsulation of the active phase. Steaming may also change the pore structure of the support. At somewhat lower temperatures the action of water vapour may result in an irreversible decrease in the surface area.

3. PHYSICAL PROPERTIES

3.1 Total surface area

Many catalysts are porous solids of high surface area and with such materials it is often useful to distinguish between the external and internal surface. The external surface is usually regarded as the envelope surrounding discrete

particles or agglomerates, but is difficult to define precisely because solid surfaces are rarely smooth on an atomic scale. It can be taken to include all the prominences plus the surface of those cracks, pores and cavities which are wider than they are deep. The internal surface comprises the walls of the rest of the pores, cavities and cracks. In practice, the demarcation is likely to depend on the methods of assessment and the nature of the pore size distribution. The total surface area (A_s) equals the sum of the external and internal surface areas. The roughness of a solid surface may be characterized by a roughness factor, i.e. the ratio of the external surface to the chosen geometric surface.

Gas adsorption methods are often used to determine the surface area and pore size distribution of catalysts. The Brunauer-Emmett-Teller (BET) adsorption method is the most widely used standard procedure. (See: Pure and Applied Chemistry 57,603 (1985)).

3.2 Pore structure

Most catalysts of high surface area are to some extent porous. Porosity is a concept related to texture and refers to the pore space in a material. It can be defined as the fraction of the bulk volume that is occupied by pore or void space. An open pore is a cavity or channel communicating with the surface of a particle, as opposed to a closed pore. Void is the space or interstices between particles.

The pore systems of solids are of many different kinds. The individual pores may vary greatly both in size and in shape within a given solid, and between one solid and another. A feature of special interest for many purposes is the width (w) of the pores, e.g. the diameter of a cylindrical pore, or the distance between the sides of a slit-shaped pore.

It is expedient to classify pores according to their sizes:

- (i) Pores with widths exceeding about 50 nm are called macropores;
- (ii) Pores with widths not exceeding 2 nm are called micropores;
- (iii) Pores of intermediate size are called mesopores.

These limits are to some extent arbitrary. It is worth emphasizing that amongst solids as a whole a wide and continuous range of pore sizes is to be found, from macropores through mesopores and micropores to grain boundaries, cleavage planes and dislocations.

The total pore volume, V_p , sometimes called specific pore volume when referred to unit mass, is the total internal volume per unit mass of catalyst. Some of this pore volume may be completely enclosed and thus inaccessible to molecules participating in a catalytic reaction. The total accessible pore volume is often derived from the amount of vapour adsorbed at a relative pressure close to unity, by assuming that the pores are then filled with liquid adsorptive. The accessible pore volume may be different for molecules of different sizes. It may be useful to determine the dead space by means of a nonsorbable gas (normally helium) in conjunction with the determination of the bulk volume of the catalyst by means of a non-wetting liquid (mercury).

The pore-size distribution is the distribution of pore volume with respect to pore size. It is an important factor controlling the diffusion of reactants and products in the porous catalyst and thus an essential property for its characterization. The computation of pore size distribution involves a number of assumptions and therefore reporting of the data should always be accompanied by an indication of the method used for its determination. (See: Pure and Applied Chemistry 57,603 (1985)).

The pore geometry of the majority of catalysts consists of an interconnected three-dimensional network of interparticle spaces, pores or capillaries. Usually capillary segments of different shapes and sizes are distributed over the network in some irregular fashion. When a solid is formed by aggregation of primary, non-porous particles, the detailed shapes of pores will depend on the size distribution of the primary particles and on their mode of packing. Platelets will tend to form wedge-shaped pores or slits. With spheres, the closeness of packing will depend on the average number of neighbours. Well defined geometrical networks can be assigned to some catalysts, e.g. zeolites, some lamellar materials, and fibrous silicates. However, the pore structure of many materials used as catalyst supports present a highly irregular geometry, far removed from simple models. This complexity imposes a serious

limitation on the reliability of the methods of calculation of pore-size distribution.

Some porous solids expand on exposure to the vapours of adsorptives. This phenomenon is called swelling. By determining the length or volume of a specimen of the solid at different vapour pressures the expansion isotherm may be obtained. Rigid adsorbents, like charcoal or silica gel, swell by only a few percent, but non-rigid adsorbents, like agar-agar, may swell to several times the original size. Provided the adsorption occurs slowly the rigid solid may accommodate the stresses, but if suddenly exposed to high vapour pressure the material may shatter.

3.3 Density

Several catalyst densities are used in the literature. True density may be defined as the mass of a powder or particle divided by its volume excluding all pores and voids. In a strict physical sense, this density can be calculated only through X-ray or neutron diffraction analysis of single crystal samples. The term apparent density has been used to refer to the mass divided by the volume including some portion of the pores and voids, and so values are always smaller than the true density. This term should not be used unless a clear description is given of what portion of the pores is included in the volume. So-called helium densities determined by helium expansion are apparent densities and not true densities since the measurement may exclude closed pores.

Bulk density, or packing density, includes all pores and voids (interparticle spaces) in its calculation. It is determined by filling a graduated cylinder, with or without tapping. It follows that the value obtained is dependent upon the form of the catalyst (powder, tablets, extrudates) because of the different contribution of interparticle void space to the pore volume. Tap density is the apparent density of a bed of particles in a container of stated dimensions when a given amount of powder is vibrated or tapped under controlled conditions. The use of the term bulk density should be encouraged, accompanied by the detailed description of the conditions of its determination.

Catalyst manufacturers also define an effective solid density, determined by displacement of a given liquid (water, ethanol). Values obtained with different liquids may vary substantially, depending on the extent to which the molecules of the liquid are able to penetrate into the pores of the catalyst. The term piece density is sometimes used when the measurement is performed with a liquid which does not substantially penetrate into the pores.

3.4 Mechanical strength

It is desirable for commercial catalysts to have sufficient mechanical strength so that losses during handling and use are minimized. Broken pieces and fines (fine powder) lost during handling or produced during commercial use can represent a significant expense, especially for catalysts containing precious metals such as Pt and Re. Depending on the design of the commercial reactor, broken catalyst, or fines, can lodge in support screens or in containment screens causing a restriction in the flow of reactants and products through the reactor. Various laboratory tests have been designed to provide information concerning the ability of a catalyst to maintain its physical integrity.

Crush strength is defined as the resistance of formed catalysts to compressive forces. Measurements of crush strength are intended to provide an indication of the ability of the catalyst to maintain its physical integrity during handling and use. When crush strength is measured for single pieces it is called piece crush strength, and when it is measured for a bulk sample it is called bulk crush strength. Other terms which have been used for piece crush strength, but which are not recommended are static crush strength and single pellet crush strength.

Piece crush strength is commonly measured by placing individual catalyst pieces between two flat surfaces, applying a compressive load, and measuring the force required to crush the piece. Best results are obtained for regular shapes, such as beads and tablets. Crush strength measurement of extrudates is less straightforward, and the results will vary greatly with particle geometry and with the details of the analytical procedures used. The procedure used should be described in detail. Some methods may be repeatable within a

single laboratory but irreproducible between laboratories.

Bulk crush strength is commonly measured by placing a representative sample in a cylinder, applying a constant force with a piston, and measuring the amount of fines generated. Many different variants are possible and no generally accepted method is yet available. The bulk crush strength is defined empirically and the results are expressed on an arbitrary scale. This measurement may be applied to all catalyst shapes.

Attrition is defined as loss of catalyst during handling or use. Attrition can occur by loss of fines through abrasion, which is wearing, grinding, or rubbing of the particles with each other or with container walls. Attrition can also occur by loss of pieces due to breakages, which can be caused by impact or collision of particles with container walls. Numerous tests have been designed to measure the resistance of catalyst particles to attrition. These tests vary considerably in complexity and severity. Their applicability depends on the particular type of catalyst being tested.

A simple method to measure attrition is to place a representative sample of the catalyst in a closed container, vibrate or shake the container, and then measure the amount of fines generated. Another relatively mild method is to place a sample in a drum having a single baffle, rotate the drum for a fixed period of time, and then measure the amount of fines generated by sieving through a standard sieve. Larger particles of silica and alumina will hold very fine particles on their surface and these stay attached during sieving, but can be removed by agitation in water.

More severe tests are applicable to catalysts used in moving bed reactors. Some tests use a high velocity stream of gas to cause attrition of the catalyst. In some tests, a small-scale plant which simulates the commercial plant is used. The amount of attrition measured in all these tests is very dependent on the exact procedure used. Reproducibility among laboratories is only likely to be possible if precise details of the method are given.

4. FINE STRUCTURE

4.1 Surface structure and topography

The catalyst particle is usually a complex entity composed of a porous solid, serving as the support for one or more catalytically active phase(s). These may comprise clusters, thin surface mono- or multilayers, or small crystallites. The shape, size and orientation of clusters or crystallites, the extension and arrangement of different crystal faces together with macrodefects such as steps, kinks, etc., are parameters describing the surface topography. The type of atoms and their mutual positions at the surface of the active phase or of the support, and the type, concentration and mutual positions of point defects (foreign atoms in lattice positions, interstitials, vacancies, dislocations, etc.) define the surface structure.

The determination of the surface structure of solid is possible using a variety of experimental methods, the methods chosen being dependent on the specific information required. Information on surface elemental composition is also desirable.

With single crystals the symmetry of the surface structure and the presence of features, such as steps, can be obtained using low energy electron diffraction (LEED). For real crystals, surface topography can be investigated by conventional optical microscopy and various other microscopic techniques, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), high resolution electron microscopy (HREM), and analytical electron microscopy (AEM).

The basic concept in examining samples by SEM is that the intensity of the radiation emerging from each region on the surface is characteristic of the topography of the region. Local variation in surface topography, i.e. orientation of the surface with respect to the electron beam gives rise to contrast in SEM. The accompanying X-ray signals generated may be used to provide information on chemical composition (energy dispersive analysis by X-rays, EDAX). The local environment of atoms (coordination number, nature of coordinating atoms and atom-to-atom distances)

can be determined from an analysis of the extended X-ray absorption fine structure (EXAFS), and that of surface atoms by using surface EXAFS (SEXAFS), glancing angle or reflection EXAFS (REFLEXAFS) or critical angle EXAFS.

4.2 Surface area of different phases

For any given catalytic reaction the active surface area is normally only a small fraction of the area of the active component (active phase). The term active sites is often applied to the sites effective for a particular heterogeneous catalytic reaction. The terms active site and active centre are often used as synonyms, but active centre may also be used to describe an ensemble of sites at which a catalytic reaction takes place. There is evidence that the centres required for some catalytic reactions are composed of a collection of several metal atoms (ensemble). This appears to be the case for such reactions as, for example, hydrogenolysis, hydrogenation of CO, and certain deuterium-exchange processes with hydrocarbons.

It is frequently convenient to describe the chemical properties of a catalyst surface by reference to surface sites. A surface site may be composed of one or more surface atoms or ions and may act as an active site for a given catalytic reaction, or may be inactive. It is characterized by the chemical reactivity of these atoms or ions and by their spatial arrangement at the surface. The site density is the number of sites per unit surface area. However, it is expedient to extend the use of this term to cases where surface area has no clear significance. In these cases the site density is referred to unit mass or unit volume of the catalyst.

In supported catalysts the surface area of the active phase is different from the total surface area. In the particular case of supported metal catalysts several techniques may be used to estimate the surface area of the active phase and the number of exposed metal atoms. (Note, however, that this does not necessarily provide a measure of the active surface area). The method used most often is based on selective chemisorption of appropriately chosen probe molecules (H_2 , CO, N_2O), the chemisorption data obtained under well defined conditions being then compared with the total surface area determined from the analysis of physical adsorption data. However, assumptions must be made regarding the stoichiometry of the interaction of the probe molecule with the surface metal atoms and of the number of surface metal atoms per unit surface area. This method provides consistent measurements of the surface area of metal particles but is not generally applicable to nonmetal catalysts.

A variation of this method consists in the titration of an adsorbed species (e.g. oxygen) by a reactant (e.g. H_2). It is still necessary to make some assumptions concerning the stoichiometry of the titration reaction.

The degree of dispersion is defined as the fraction (percentage) of the total metal atoms which are surface atoms. (The term fraction exposed (percentage exposed) is synonymous with the degree of dispersion).

Several physical methods may be used to provide indirect estimates of the degree of dispersion. Sizes of particles, or of single crystallites, or of magnetic domains determined, respectively, by electron microscopy, X-ray line broadening, and magnetization measurements, can be used for this purpose but, in all cases, assumptions must be introduced into the calculations.

An alternative means of description is to use the mean diameter of primary particles as obtained from low-angle X-ray scattering, broadening of X-ray diffraction lines or EXAFS. It may also be possible to use these techniques to determine the grain size of the support, or of the catalyst particles in general, providing these materials are sufficiently crystalline. The particle-size distribution may be measured directly using one of the microscopic techniques or indirectly by using a sedimentation method.

4.3 Surface elemental composition of different phases

The chemical nature and composition of catalyst surfaces are essential parameters for understanding catalytic reactivity. Electron spectroscopies, mainly Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectroscopy (SIMS) and Ion Scattering Spectroscopy (ISS) allow such information to be obtained. AES and XPS are most likely to provide meaningful data if the surface region of the solid is homogeneous over a depth several times the inelastic mean free path of the emitted electrons.

In catalysis it is important not only to be able to study the surface region of the catalyst itself, but also any adlayer that may be present. The latter may arise from adsorption or preferential segregation of one component from the bulk to the surface. The spatial distribution of the elements at the surface can be obtained from scanning AES. Experiments, in which the surface is progressively eroded, e.g., by ion-bombardment, with surface analysis by AES, XPS or ISS carried out after various times, may provide concentration-depth profiles of the chemical species.

4.4 Surface chemical characterization

The activity of a catalyst depends on the nature, the number, the strength and the spatial arrangement of the chemical bonds that are transiently created between the reactants and the surface. The objective of the chemical characterization of the surface is a detailed description of the adsorbate-adsorbent bonds that a given catalyst will develop when contacted with a given reaction mixture. Therefore, chemical characterization should be done in situ in the course of the reaction itself. However, because of experimental limitations, this is seldom possible and catalyst surfaces are usually characterized by means of separate experiments. It is important to characterize the catalyst surface both before and after its use in a reaction.

The pretreatment of the catalyst, before the chemical characterization experiments, must be selected so that the relevant surface properties are as similar as possible to those existing during the catalytic reaction. When the chemical constitution of the surface or its structure are not significantly modified by the reaction itself, the same pretreatment can be used for the characterization experiments as for the catalytic tests.

Ideally, the probe molecules used in the chemical characterization experiments should simulate as closely as possible the behaviour of the actual reactants. This is rarely possible and so simple probe molecules (H_2 , O_2 , CO, NO) are used instead. Some additional information about the nature of the surface may be obtained using thermal analysis methods, e.g., calorimetry, temperature-programmed desorption, temperature-programmed reaction.

When a catalytic reaction modifies the surface properties of the catalyst in a way which cannot be simulated in the absence of reactants, or when large series of similar catalysts are to be compared, it is convenient to characterize a given catalyst by its activity in an appropriate probe-reaction

4.4.1 Acid-base sites

An acid-base surface contains individual acidic and basic sites which may interact together. On a given surface, one type (acidic or basic) may prevail but both are always present (conjugate acidic and basic pairs). Examples of such surfaces are found in metal oxides, sulfides and other compounds. The description of acidic and basic surface properties requires the determination of the nature (Lewis or Brønsted), the density, the location, and the strength distribution of sites. It is important to distinguish between the number of acid (or base) sites and the acid (or base) strength distribution.

Acidic and basic sites are usually generated during the catalyst synthesis but many pretreatments can change the number, the nature and/or the strength of the sites. Such changes may result, for instance, from: decomposition of ammonium or organic cations, ion exchange, reduction or oxidation of cations, hydration-dehydration, dehydroxylation by reagents in solution, upon heating or evacuation, water decomposition on polarizing cations, steaming, exposure to various gases, (e.g. Cl_2 , CO_2 , H_2S , F_2), treatment with chemicals (dealumination). Therefore, the choice of specific and defined conditions for characterization is of major importance.

No rigorous practical definition of acid strength exists outside of very dilute aqueous solutions where activity coefficients can be assumed to be unity. Each method of measuring the acid strength of surface sites is liable to give somewhat different answers, the results being qualitative at best. The dielectric constant of the medium, in which the acid or base probe is used influences the measured acid-base strength.

In general terms, an acidic site may be defined as a site on which a base is chemically adsorbed, and basic site as a site on which an acid is chemically

adsorbed. A Brønsted acid shows a tendency to donate a proton and the Brønsted base to accept a proton. A Lewis acid is able to accept an electron pair and a Lewis base to donate an electron pair. The Lewis acid can be, for instance, a coordinatively unsaturated aluminium ion in alumina or silicoaluminates, a cation such as Na(I) or Ca(II) in zeolites, etc.

The acid or base strength is defined by comparing the interaction between the sites and reference (probe) molecules. For example, the acid strength is the ability of the site to convert an adsorbed reference neutral base into its conjugate acid. This process may be monitored by following the colour changes of the indicators or by such techniques as IR or NMR spectroscopies. Several criteria must be considered in the selection of these probes: their pK value must be adapted to the acidity or basicity of the surface under study; the size of the probe molecules should ensure that all sites are readily accessible; finally, the probe should be selected so that its interaction with the surface is easily studied by the available experimental techniques. Catalytic test reactions are sometimes used for the evaluation of acid-base properties of catalysts. For example, dehydration of propan-2-ol is a convenient test for weak surface acidity.

Since acidic or basic sites may interact with each other, the site density ought to be determined. Moreover, an attempt should be made to describe the site location, particularly in the case of microporous acid catalysts (zeolites).

4.4.2 Redox sites

Redox sites may be separated into two categories, namely (i) sites incorporating atoms which, in the presence of the reactants, are oxidized or reduced, and (ii) sites able to form a charge-transfer complex by interaction with an electron acceptor or an electron donor.

In the case of surface sites incorporating atoms, the valence states and their eventual variation in the course of the reaction can be studied by spectroscopic methods such as electron paramagnetic resonance (EPR), XPS, ultraviolet photoelectron (UPS), IR, and near-edge X-ray (XANES) spectroscopies. (see Note b)

Quantitative information on the number of sites may be obtained from a volumetric or gravimetric study of the adsorption of oxidizing or reducing molecules. Adsorption calorimetry can be used to determine the energetics of the site distribution, as in the case of acidic and basic sites.

The formation of a charge-transfer complex is related to the ionization potential (E_i) of the electron-donor, to the electron affinity (E_{ea}) of the electron acceptor and to the dissociation energy (E_d) of the complex:



The number of ionized species is given by $N_i = N \cdot \exp [-(E_i - E_{ea} - E_d)/(kT)]$

In the case of some paramagnetic molecules, the formation of a charge-transfer complex can be determined by EPR either directly, when the electron of the donor molecule interacts with the nuclear spin of the electron-acceptor site, or indirectly by observation of the electron delocalisation in the probe molecule. Both methods can yield quantitative information about the distribution of electron donor or electron acceptor sites when a range of probe molecules having different electron affinities or ionization energies are used.

5. CATALYTIC PROPERTIES

5.1 General considerations

In heterogeneous catalysis a fluid (liquid or gas) is brought into contact with a solid catalyst, which effects a change of chemical composition of the fluid ideally without itself entering into the stoichiometric equations. Catalysis by solids can be observed only through the chemical change in the fluid which is in contact with the catalyst, the system being either closed or open. The system is called open when it exchanges matter and energy with its surroundings. The quantitative measure of catalytic properties is then based on the material balance of the system (the system could be defined as a catalyst bed, catalyst particle, an element of active surface or an active site) to which reactants are introduced and products removed, preferably at

Note b: Near-edge X-ray spectroscopy is abbreviated in some parts of the world, particularly in USA, as NEXASS.

the steady state, when the catalyst is neither a net source nor a sink of material. The criterion used to define the steady state should be stated.

Quantitative description of catalytic properties requires that the system under consideration be unambiguously described with respect to system boundaries (mass of catalyst m_c , area of catalytic surface A_c , or volume of porous catalytic particle V_c) and conditions such as composition, pressure, temperature, prevailing at the boundary (control variables). A set of data characterizing a catalyst must permit the prediction of material balance of the system containing the catalyst at steady state under at least one set of control variables. It is sometimes possible to represent a number of experimental observations by rate equation or a set of rate equations which may or may not be based on a mechanistic model. The model has to fulfil the above criteria within a certain range of validity which should be indicated. The catalytic system should be characterized with respect to the rate of chemical change (activity) and with respect to product composition (selectivity).

5.2 Catalytic activity

5.2.1 Reaction rate

We distinguish integral and differential characteristics of catalytic properties. One of the integral characteristics is the extent of reaction ξ . Generally, any chemical reaction, whether overall or an elementary step, can be represented by a stoichiometric equation:

$$\sum \nu_i B_i = 0$$

where ν_i is the stoichiometric coefficient of component B_i , taken positive when B_i is a product and negative when it is a reactant. The chemical change ξ occurring in the course of the reaction may be described by ξ (in mol):

$$\xi = \frac{n_i - n_{i0}}{\nu_i}$$

where n_{i0} and n_i are the amounts of substance B_i (in moles) at time zero and at any t time, respectively. It is an extensive quantity attained under specified conditions.

An alternative expression is its dimensionless form, having a value between zero and unity, called fractional conversion or degree of conversion.

The drawback of integral characteristics such as extent of reaction or degree of conversion is that very many control variables such as the reactor type, feed composition, time, temperature, etc., influence the values obtained and have to be standardized. Moreover, with high conversion, a great difference in catalytic activity usually leads to only small differences in the conversion values.

A differential characteristic which demands a lower degree of standardization is the reaction rate. The rate of a chemical reaction with respect to compound B at a given point is defined as the rate of formation of B in moles per unit time per unit volume. It cannot be measured directly and is determined from the rates of change of some observable quantities such as the amount of substance, concentration, partial pressure, which are subject to measurements. Reaction rates are obtained from observable quantities by use of the conservation equations resulting from the mass balance for the given reactor type.

The conservation equation for component B_i , for any system, can be written as

$$F_{i,0} = F_i + F_{i,c} + (dn_i/dt)$$

where $F_{i,0}$ = flow rate of component B_i into the system in $\text{mol}\cdot\text{s}^{-1}$
 F_i = flow rate of component B_i out of the system in $\text{mol}\cdot\text{s}^{-1}$
 $F_{i,c}$ = rate of consumption of component B_i by reaction inside the system in $\text{mol}\cdot\text{s}^{-1}$
 t = time

For an ideal gradientless flow reactor (continuous stirred tank reactor CSTR) in the steady state the conservation equation reduces to

$$\underline{r} = - \underline{v}_i^{-1} (\underline{F}_{i,0} - \underline{F}_i) / \underline{Q}$$

where \underline{r} is the reaction rate in $\text{mol} \cdot \text{s}^{-1}$ per unit amount of catalyst and \underline{Q} is the amount of catalyst.

For an ideal plug flow reactor the mass balance in the steady state gives

$$\underline{r} = - \underline{v}_i^{-1} d\underline{X} / d(\underline{Q} / \underline{F}_{i,0})$$

where \underline{X} is the fractional conversion, and the term $\underline{\tau}$ (in units of time per amount of catalyst per amount of reactant)

$$\underline{\tau} = \underline{Q} / \underline{F}_{i,0}$$

is called the space time. The inverse of the space time is the space velocity

$$\underline{v} = \underline{F} / \underline{Q}$$

frequently expressed in h^{-1} (gas or liquid hourly space velocity, GHSV or LHSV, respectively), if the quantities of catalyst and reactants are expressed in the same units.

In the case of ideally stirred batch reactor the mass balance leads to the expression

$$\underline{r} = \underline{v}_i^{-1} (d\underline{n}_i / dt) / \underline{Q}$$

As the true state variable of the system the rate \underline{r} depends only on the temperature and concentration if it is derived from data free of heat and mass transfer effects.

The reaction rate under specified conditions (composition, temperature, pressure) is a measure of the catalytic activity of the solid for conversion of B under these conditions. The amount of catalyst \underline{Q} to which the reaction rate is referred may be expressed by the mass (\underline{m}_C), volume (\underline{V}_C) or the surface area (\underline{A}_C) of the solid catalyst. Correspondingly the values obtained are

<u>mass-specific rate</u>	\underline{r}_m in $\text{mol} \cdot \text{s}^{-1} \cdot \text{kg}^{-1}$
<u>volume-specific rate</u>	\underline{r}_V in $\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-3}$
<u>area-specific rate</u>	\underline{r}_A in $\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$

In spite of the fact that it was previously recommended that \underline{r}_m be called the specific activity of the catalyst (see Pure Appl.Chem. 46, 71 (1976)) the use of this term is now discouraged.

A rate equation describes the observed dependence of the rate of reaction on the composition of the fluid phase at the boundary of the system under consideration (e.g., catalyst particle, element of surface). The coefficients of the rate equation must be given in proper units so that a material balance of the system under consideration can be predicted unambiguously within the range of control variables over which validity of the rate equation is postulated. These rate coefficients \underline{k} (the experimental rate constants) may be taken to characterize the catalytic activity.

For a single elementary reaction,

$$\underline{k} = \underline{A} \cdot \exp[-\underline{E} / (\underline{R}\underline{T})]$$

where \underline{A} is the pre-exponential factor and \underline{E} is the activation energy. Where an overall catalytic reaction obeys the Arrhenius equation over a certain range of temperatures the experimentally determined energy is an apparent activation energy.

A rate equation in terms of the local composition of reacting fluid in contact with the surface of the catalytically active material may be called the "intrinsic" rate equation; the coefficients in this equation are "intrinsic" rate coefficients. The local concentrations of reactants and products at the catalytic surface in general cannot be observed and have to be inferred from

the observable composition at the boundary of a larger system, the observed rate of reaction and the kinetics of mass transfer between the boundary of the larger system and the active surface under consideration.

The turnover frequency, N , (the term turnover number is discouraged) is defined as the number of molecules reacting per active site in unit time. It is necessary to specify the method used to estimate the number of active sites. Usually, the number of active sites will be assumed to be equivalent to the number of surface atoms, derived, in the case of metals, for example, from measurements of the chemisorption of a specified adsorptive.

5.2.2 Measurement of activity parameters

Rates of reaction depend in general on the composition and on the temperature of the fluid surrounding the catalytically active solid. These quantities must be observed simultaneously for a catalyst particle in order to describe its catalytic activity.

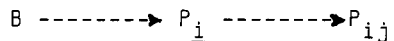
Simultaneous measurements of the rate of change, temperature and composition of the reacting fluid can be reliably carried out only in a reactor where gradients of temperature and/or composition of the fluid phase are absent or vanish in the limit of suitable operating conditions. The determination of specific quantities such as catalytic activity from observations on a reactor system where composition and temperature depend on position in the reactor requires that the distribution of reaction rate, temperature and composition in the reactor are measured or obtained from a mathematical model, representing the interaction of chemical reaction, mass-transfer and heat-transfer in the reactor. The model and its underlying assumptions should be specified when specific rate parameters are obtained in this way.

The spatial distribution of composition and temperature within a catalyst particle or in the fluid in contact with a catalyst surface result from the interaction of chemical reaction, mass-transfer and heat-transfer in the system which in this case is the catalyst particle. Only composition and temperature at the boundary of the system are then fixed by experimental conditions. Knowledge of local concentrations within the boundaries of the system is required for the evaluation of activity and of a rate equation. They can be computed on the basis of a suitable mathematical model if the kinetics of heat- and mass-transfer are known or determined separately. It is preferable that experimental conditions for determination of rate parameters should be chosen so that gradients of composition and temperature in the system can be neglected.

The effectiveness factor of a porous catalyst is the ratio of the rate of reaction to the hypothetical rate which would be expected if fluid composition and temperature in the pores corresponded to composition and temperature in the fluid surrounding the porous aggregate.

5.3 **Selectivity**

Very often a reactant or a set of reactants may simultaneously undergo several parallel reactions, giving different individual products, P_i , which react further in consecutive reactions to give different secondary products, P_{ij} . A commonly encountered situation is the parallel-consecutive reaction network.



It is sometimes advantageous to consider not the individual products, but the sets of products, resulting from reactions of a given type, e.g., hydrogenation, hydrogenolysis, etc. In what follows the symbol P_i will designate either the individual product or a set of products. In the \bar{i} latter case each set of products will have the same elemental composition as the reactant (or set of reactants) B.

Selectivity may be determined in the integral or differential mode. Integral selectivity depends on the overall extent of the reaction (degree of conversion) and on the type of reactor used even if heat and mass transfer effects are eliminated. It may be called reactor selectivity for the formation of product P_i from the set of reactants B when it is calculated as the mole fraction of \bar{i} P_i in the products (excluding unconverted feed) at the exit of the reactor:

$$(\underline{S}_i)_R = \frac{n_i}{\sum n_i}$$

when the feed stream consist of the set of reactants B.

An alternative expression is the ratio between the mass of P_i in the products and the total mass of products generated from B.

The yield (Y) of product P_i is defined as:

$$Y = \frac{\text{Amount of B converted into } P_i}{\text{Amount of B introduced}} = \frac{\text{Number of molecules of B converted into } P_i}{\text{Number of molecules of B introduced}}$$

The conversion (X) of reactant B is defined as:

$$X = \frac{\text{Amount of B reacted}}{\text{Amount of B introduced}} = \frac{\text{Number of molecules of B reacted}}{\text{Number of molecules of B introduced}}$$

Alternative expressions for yield and conversion can be obtained using masses of P_i and B, respectively.

On this basis yield = (selectivity) x (conversion).

Selectivity is generally a function of conversion and will depend on the system under consideration if the relative extents of consecutive and parallel reactions depend on the spatial distribution of composition and on the residence time in the reactor.

Differential selectivity, or intrinsic selectivity of a catalytically active surface with respect to the formation of product P_i from reactant B may be evaluated as the ratio of the rate of reaction r_i resulting in product P_i and the sum of the rates of all reactions r_i . Consequently, the differential selectivity depends only on temperature and the actual concentrations of reactants but not on the reactor type used, and is more suitable for the discussion of the correlation of catalytic properties with the structure and chemistry of the catalytic system.

If the effects of operating variables on selectivity are to be expressed, instead of reaction rates r_i in the expression for differential selectivity the corresponding rate equations are introduced.

5.4 Relative activities

For a rapid characterization of a series of catalysts it is sometimes advantageous to determine their relative activities at given reaction conditions. The methods of determining relative activities may be fairly simple, but they should only be applied to a family of similar catalysts in which case the mechanism of the test reaction can be assumed not to change. Then it is possible to compare the values, e.g., of the time variable necessary to obtain the same degree of conversion with the same starting reaction mixture. This is more justified than comparing the conversions obtained at the same reaction time or space time. The alternative is to determine the temperature at which different catalysts give the same degree of conversion under the same initial composition and time variable; this approach is closer to the operation of an industrial reactor. The reciprocal values $1/I$ are compared, although the relationship between $1/I$ and the relative activities is not rigorously linear even for reactions with the same mechanism and activation energy.

5.5 Inhibition of the catalytic action

5.5.1 Types of inhibitory substances

The activity of practically all catalysts can be partially or totally inhibited by inhibitory or deactivating substances, in a broad sense. In what follows such a substance will be indicated by IS. This can be caused by: adsorption of IS more strongly than reactants on active sites (as); change of

as due to reaction with IS: restriction of physical access due to formation of a (semi) impervious layer of IS.

The IS may (i) be present in the reactants as impurities, (ii) come from other sources (equipment, etc.) or (iii) be formed during the course of the reaction (by transformation of intermediary or final products, etc.).

Ideally, the characterization of catalysts with respect to inhibition should involve 3 types of information:

1. nature of the IS acting on the catalyst,
2. adequate relationship between the quantity of IS and catalytic properties,
3. time-dependent effects on activity, selectivity, etc., due to the presence, or a modification of concentration, of IS (decreases of catalytic activity with time, total or partial recovery of catalytic properties after removal of IS from the feed, etc.).

IS may be classified into three categories:

Poisons (true poisons) are characterized by their propensity to attach very strongly, by a true chemical bond (e.g. covalent) to the surface atoms or ions constituting the catalytically active sites. Poisons act in minute quantities. Typical poisons of metals are S, As, etc. In most cases, activity and/or selectivity cannot be recovered without a drastic change in operating conditions (most often a regeneration). Recovery, if at all, takes place very slowly and/or only partially.

Inhibitors have a transient effect (inhibition). All catalytic properties can be recovered after the supply of the inhibitor to the catalyst has been stopped, without otherwise changing the operating conditions. Inhibitors act in minute quantities, have a reversible effect and correspond to more or less strong bonding.

Fouling agents, or mechanical inhibitors are bound by neither covalent nor other strong bonds to the active centres: the interaction is usually of the van der Waals, H-bond, or sometimes ionic, type. They form protective layers or block pores, thus physically impeding access of reactants to the active centres. The fouling agents causing real problems are those which have a long standing effect and do not disappear spontaneously. Carbon deposits act, partially or totally, this way. Other examples are vanadium and nickel sulfide deposits in hydrotreating catalysts.

Fouling agents act in quantities equivalent to several layers spread over the catalyst surface or to pore volume; they may according to different cases, have a rapidly reversible, an only slowly reversible, or an irreversible effect.

5.5.2 Characterization of catalyst response to inhibitory substances

In principle, sensitivity to inhibition (by poisons, inhibitors or fouling agents) depends on the whole catalytic reaction system: nature of catalyst, degree of ageing (in particular, nature and degree of poisoning, modification of activity and selectivity by inhibition and fouling), operating conditions, etc. Accordingly, the activity and selectivity of a catalytic reaction depends on all the previous history of the catalyst.

Sensitivity to the deactivating influence of impurities, reaction products or intermediates is expressed in different ways depending on the category of deactivating agent (poison, inhibitor, fouling agent).

5.5.2.1 Poisons

Sensitivity to poisons depends on:

- number of active centres in the catalyst: when it is small, the catalyst may be inhibited by a small amount of poison;
- strength of adsorption of the poison on the active centres; the weaker is the adsorption of poison, the lesser is the sensitivity of the catalyst to poison;
- the effectiveness of adsorbed poison for inhibiting the catalytic activity; the latter decreases sometimes on adsorption of small amounts of poison on active centres more than in proportion to the fraction of active centres covered by the poison.

Sensitivity to poisons may be defined by:

1. the minimum amount of poison X_0 per unit amount of catalyst required to eliminate the catalytic activity (sometimes called the lethal dose). If the number of active centres per unit mass of catalyst, X_t , is known, the quantity X_0/X_t should be recommended as the measure of the sensitivity of the catalyst to the poison in question.
2. the initial ratio of the fractional decrease in the catalytic activity ($\alpha = (a_0 - a_p)/a_0$) to the amount of poison n_p attached to the catalyst per unit mass, α/n_p (where a_0 is the activity of the catalyst in the absence of poison and a_p is the activity in the presence of poison). This ratio may be called initial sensitivity. Sometimes the ratio α/c_p is used instead, where c_p is the concentration of the poison in the feed. This definition is not encouraged.

5.5.2.2 Inhibitors

There is actually a whole spectrum of possible phenomena, between very strong irreversible poisoning and normal competition between molecules for a given site (this competition leading to a decrease of activity). Inhibitors, as defined above, correspond to a behaviour intermediate between those just mentioned. The sensitivity to inhibitors can thus be expressed either as in the case of true poisons, or as in the case of competition. In the latter formulation, for example, the value or relative value, of the adsorption coefficient could characterize the inhibitor.

It is advisable to define also the rate at which activity decays when the catalyst is contacted with a given concentration of inhibitors, or recovers, after addition of the inhibitor is discontinued.

5.5.2.3 Fouling agents

The inhibiting influence of fouling agents is not a simple function of the quantity of deposited substance. The reason is that the relationship between this quantity w and activity depends on the nature and texture of the catalyst, the nature and concentration of the feed constituents, temperature and operating conditions, and the rate of build-up of the fouling deposit. With this restriction the sensitivity to fouling agents is defined as the quantity necessary to bring about a given effect on activity or selectivity.

5.6 Time-dependent characteristics

The composition, structure, texture, surface state, activity and selectivity of catalysts change continuously, at rapid or slow rates according to conditions, with time-on-stream. This change is characteristic of each catalyst, and depends on its formulation, preparation and previous history. Deactivation is one aspect. Another is the usually rapid changes that catalytic activity and selectivity undergo in the first few minutes, hours or sometimes days of operation: this may be called the initial adjustment to catalytic operation. A third aspect is the response to changing operating conditions (response to change).

The time-dependent changes of a catalyst are due to processes belonging to 6 main categories:

- (a) poisoning;
- (b) inhibition;
- (c) fouling;
- (d) sintering;
- (e) chemical reactions;
- (f) remodelling of the surface.

Poisoning, inhibition and fouling have already been defined. Sintering refers to the diminution of dispersion. All phases present in a catalyst (active phases, modifiers, support) potentially can undergo sintering.

Chemical reactions comprise reaction with feed intermediates or final products and reaction between catalyst components. They may result in the addition of material to the catalyst or its loss, by formation of a volatile compound.

Remodelling refers to changes of the surface which do not involve any of the previous processes: migration of active species inside a catalyst pellet,

change of shape (independently from change of total surface area developed) of crystallites of a given phase, change in the number of steps, kinks on a surface, changes in surface/bulk composition ratio.

5.7 Regeneration

The performance of deactivated catalysts can often be improved by regeneration. Deactivation results from inhibition, from fouling and from sintering and all of these may be reversed - at least in part - with some catalysts.

It follows that regeneration may consist of either (i) removal of IS; sometimes poisons, most often inhibitors or fouling agents, e.g., coke (hydrogenation catalysts, e.g., selective hydrogenation of pyrolysis gasoline) or (ii) redispersion of the active species (platinum catalysts) or (iii) both (hydrodesulfurization or catalytic reforming catalysts).

REFERENCES

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