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MANUAL OF METHODS AND PROCEDURES FOR CATALYST CHARACTERIZATION

(Technical Report)

Prepared for publication by

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Manual of methods and procedures for catalyst characterization (Technical Report)

Synopsis. The manual provides details and recommendations concerning the experimental methods used in catalysis. The objective is to provide recommendations on methodology (rational approaches to preparation and measurements). It is not intended to provide specific methods of preparation or measurement, nor is it concerned with terminology, nomenclature, or standardization.

TABLE OF CONTENTS

1. INTRODUCTION

2. CATALYST PREPARATION

2.1 Preparation of the Primary Solid

2.1.1. Deposition

2.1.1.1. *Impregnation*

2.1.1.1.A. Impregnation by soaking, or with an excess of solution [2]

2.1.1.1.B. Dry or pore volume impregnation

2.1.1.1.C. Incipient wetness impregnation

2.1.1.1.D. Deposition by selective reaction with the surface of the support

2.1.1.1.E. Impregnation by percolation

2.1.1.1.F. Co-impregnation

2.1.1.1.G. Successive impregnation

2.1.1.1.H. Precipitation-deposition (see 2.1.2.2.)

2.1.1.2. *Ion exchange*

2.1.1.3. *Gas phase deposition*

2.1.1.4. *Solid-solid reactions*

2.1.1.5. *Wash coat*

2.1.2. Precipitation and co-precipitation

2.1.2.1. *Synthesis of zeolites and related materials*

2.1.2.2. *Precipitation-deposition*

2.1.3. Gel formation and related processes

2.1.4. Selective removal

2.1.5. Pillared layer compounds

2.2. Treatment of intermediate solids or precursors

2.3. Activation of the precursor

2.4. Forming methods

2.4.1. Powder: preparation, crushing and grinding

2.4.2. Forming by crushing

2.4.3. Spray drying

2.4.4. Oil drop

2.4.5. Granulation

2.4.6. Tabletting

2.4.7. Extrusion

2.5. Stability during handling and storage

2.5.1. Activated catalysts

2.5.1.1. *Passivation*

2.5.1.2. Protection by an inert gas

2.5.1.3. Protection by a condensed phase

3. CHARACTERISATION OF SURFACE PROPERTIES BY ADSORPTION METHODS

3.1. Methodology

3.1.1. Static methods

3.1.2. Dynamic methods

3.1.3. Desorption

3.1.4. Precautions

3.2. Categories of catalysts

3.2.1. Metals [12-16]

3.2.2. Acidic amorphous oxides and zeolites

3.2.3. Sulfides

4. FINE STRUCTURE OF CATALYSTS [20]

4.1. Surface structure and chemical composition

4.2. Surface structure and topography

4.2.1. Electron microscopy

4.2.1.1. *Conventional transmission electron microscopy (CTEM)*

4.2.1.2. *Techniques related to CTEM*

4.2.1.2.A. Dark field methods

4.2.1.2.B. High resolution electron microscopy (HREM)

4.2.1.2.C. Reflection electron microscopy (REM) and reflection high energy electron diffraction (RHEED)

4.2.1.2.D. Scanning electron microscopy (SEM) [21]
4.2.1.2.E. Scanning transmission electron microscopy (STEM) [22]
4.2.1.2.F. Selected area diffraction (also called: microdiffraction)
4.3. X-ray and neutron methods for structure determination
4.3.1. X-ray diffraction and diffusion
4.3.2. Radial electron distribution (RED)
4.3.3. Extended X-ray absorption fine structure (EXAFS) [20]
4.3.4. Techniques related to EXAFS
4.3.5. Neutron diffraction
4.4. Ion scattering techniques
4.5. Electron state and local environment of elements
4.5.1. Nuclear magnetic resonance (NMR) (20)
4.5.2. Electron spin resonance (ESR)
4.5.3. Mössbauer spectroscopy
4.6. Vibrational spectroscopies
4.6.1. Transmission infrared spectroscopy (IR)
4.6.2. Infrared emission spectroscopy
4.6.3. Diffuse reflectance spectroscopy (DRS)
4.6.4. Internal reflectance spectroscopy
4.6.5. Photoacoustic spectroscopy (PAS)
4.6.6. Others
4.6.7. Raman spectroscopy
4.6.8. Inelastic neutron scattering spectroscopy (INS)
4.8. Electron spectroscopies
4.8.1. Photoelectron spectroscopy (XPES, UPES)
4.8.2. Auger electron spectroscopy (AES)
4.9. Determination of spatial distribution of elements
4.9.1. Analytical electron microscopy
4.9.2. Energy dispersive X-ray spectroscopy (EDS, EDX)
4.9.3. Electron energy loss spectroscopy (EELS)
4.9.4. Scanning Auger microscopy (SAM)
4.10. Secondary ion mass spectroscopy (SIMS)
4.11. Ion beam techniques (see also section 4.5)
4.12. Depth profiling

5. CATALYTIC PROPERTIES
5.1. Reactor types and measurement methods [38]
5.1.1. Plug flow reactor
5.1.2. Continuous stirred tank reactor (CSTR)
5.1.3. Fluidized bed reactor
5.1.4. Batch reactor
5.1.5. Discontinuous flow reactor
5.1.6. Reactants - Introduction methods
5.1.7. Typical experimental parameters used in catalyst testing
5.1.7.1. *Reactor*
5.1.7.2. *Reactants*
5.1.7.3. *Catalyst*
5.1.7.4. *Problems of heat and mass-transfer*
5.2. Kinetic analysis [39-47]
5.2.1. Determination of the reaction rate
5.2.2. Rate equations
5.2.3. Selection of a suitable form of the rate equation and evaluation of constants
5.2.4. Heat and mass transfer effects
5.2.4.1. *Internal mass and heat transfer*
5.2.4.2. *External mass and heat transfer*
5.3. Inhibition of catalytic action
5.3.1. Identification of the inhibiting substances
5.3.2. Identification of the mode of action of the IS
5.3.3. Characterisation of catalysts with respect to their response to IS
5.3.4. Poisons
5.3.5. Inhibitors
5.3.6. Fouling agents
5.4. Deactivation of catalysts and time-dependent effects
5.4.1. Deactivation: overall characterization
5.4.2. Physico-chemical characterization in deactivation studies
5.4.3. Accelerated tests
5.5. Regeneration
5.5.1. Preliminary treatment
5.5.2. Removal of inhibitory substances (IS)
5.5.4. Removal of foulants
5.5.5. Redispersion
5.5.6. General

6. ACKNOWLEDGMENTS

7. REFERENCES

LIST OF ACRONYMS

1. INTRODUCTION

This manual has been prepared by the Commission on Colloid and Surface Chemistry including Catalysis of the IUPAC. It complements the Manual on Catalyst Characterisation which concerned nomenclature [1] and should be read in conjunction with this earlier manual. The Manual of Methods and Procedures for Catalyst Characterization provides details and recommendations concerning the experimental methods used in catalysis. The objective is to provide recommendations on methodology (rational approaches to preparation and measurements). It is not intended to provide specific methods of preparation or measurement, nor is it concerned with terminology, nomenclature, or standardization.

2. CATALYST PREPARATION

The long-standing experience of industry in catalyst manufacture, the progress of scientific understanding of the processes involved and the development of the corresponding basic sciences (chemistry of solids, colloid chemistry, etc.) mean that catalyst preparation is nowadays a science. That science provides well defined guidelines which are reflected in the following document.

Methods of catalyst preparation are very diverse and each catalyst may be produced via different routes. Preparation usually involves several successive steps. Many supported metal and oxide catalysts are prepared by the succession of impregnation, drying, calcination, activation; zeolite catalysts are prepared by precipitation of gel, crystallisation, washing, ion exchange, drying. The properties of heterogeneous catalysts depend on all their previous history.

Three fundamental stages of catalyst preparation may be distinguished:

* preparation of the primary solid (or first precursory solid) associating all the useful components (e.g., impregnation or coprecipitation, or, in the case of zeolites, crystallization);
* processing of that primary solid to obtain the catalyst precursor, for example by heat treatment;
* activation of the precursor to give the active catalyst: reduction to metal (hydrogenation catalysts), formation of sulfides (hydrodesulfurisation), deammoniation (acidic zeolites). Activation may take place spontaneously at the beginning of the catalytic reaction (selective oxidation catalysts).

2.1 Preparation of the Primary Solid

All experimental parameters are critical for determining the characteristics of the solid obtained after the first step:

* aggregate morphology of the carrier used, if any;
* quantities used (solutions, carrier);
* concentrations;
* stirring conditions (shape and volume of vessel are important);
* temperature and temperature changes;
* sequence and duration of all operations;

Four main routes exist for preparing the primary solid: *deposition, precipitation and co-precipitation, gel formation, selective removal.*

2.1.1. Deposition

2.1.1.1. *Impregnation*

Impregnation consists in contacting a solid with a liquid containing the components to be deposited on the surface. During impregnation many different processes take place with different rates.

* selective adsorption of species (charged or not) by coulomb force, van der Waals forces or H-bonds;
* ion exchange between the charged surface and the electrolyte;
* polymerisation/depolymerisation of the species (molecules, ions) attached to the surface;
* partial dissolution of the surface of the solid.

The type of product depends on (i) the nature of both reactants (the liquid and the solid surface), and (ii) the reaction conditions. The main parameters affecting the liquid are the pH, the nature of the solvent, the nature and concentrations of the dissolved substances. The first parameter affects ionisation and, in many cases, the nature of the ions containing the active elements. The second and third influence solvation.

The main properties of the solid are the texture, the nature of functional groups (e.g., the number and strength of the acidic and basic centres, the isoelectric point), the presence of exchangeable ions, and the reactivity (surface dissolution in acidic or basic solution, etc.).

In the overall impregnation process the following important facts should be noted:

* the properties of the liquid in the pores are different from those measured in the bulk;
* equilibrium between liquid and solid is slow to establish and even distribution of attached species inside the pores is not easy to attain;
* deposition involves many different types of interaction as described above.

Impregnation can be made by at least 8 different methods.

2.1.1.1.A. Impregnation by soaking, or with an excess of solution [2]

Excess liquid is eliminated by evaporation or by draining. Deposition of the active element is never quantitative. The quantity deposited depends on the solid/liquid ratio. Deposition is slow, requiring several hours or days. Extensive restructuring of the surface (loss of surface area, etc.) may occur. However, the method allows the distribution of the species to be very well controlled and high dispersions may be obtained. The method works best if ion/solid interactions are involved.

2.1.1.1.B. Dry or pore volume impregnation

The required amounts of components are introduced in the volume corresponding to the pore volume of the support. The method is best suited to deposition of species which interact very weakly with the surface, and for deposition of quantities exceeding the number of adsorption sites on the surface. If the number of species which can adsorb on the surface is smaller, a chromatographic effect may occur, i.e. attachment to the mouth of the pores. Redistribution inside the pores is very slow.

2.1.1.1.C. Incipient wetness impregnation

A procedure similar to dry impregnation, but the volume of the solution is more empirically determined to correspond to that beyond which the catalyst begins to look wet. All the comments under 2.1.1.1.B. above apply.

2.1.1.1.D. Deposition by selective reaction with the surface of the support

The carrier is left in contact with an excess of solution for a definite time, and then the excess liquid is removed, e.g. using a dipping technique. The objective is to make a strong bond with the surface. The process is little used but it has potential for grafting or anchoring active elements to a support.

2.1.1.1.E. Impregnation by percolation

The precursor is sorbed/ion exchanged by percolation of the impregnating solution through a bed of carrier. There is much similarity between this method and impregnation with an excess of solution (2.1.1.1.A.). The advantage is a faster approach to equilibrium. One can easily follow the progress of the process by analysing the effluent. There may be differences in the degree of deposition along the carrier bed.

2.1.1.1.F. Co-impregnation

Two or several active components are introduced in a single step. Co-impregnation with uniform distribution and without segregation of species is extremely difficult to achieve.

2.1.1.1.G. Successive impregnation

Two or several active components are introduced sequentially. Drying (and often calcination) takes place between the impregnations. For the second impregnation the properties of the surface to take into account are those of the solid obtained after the previous impregnation.

2.1.1.1.H. Precipitation-deposition (see 2.1.2.2.)

2.1.1.2. *Ion exchange*

The general comments under 2.1.1.1. remain valid.

2.1.1.3. *Gas phase deposition*

Deposition occurs by adsorption or reaction from a gas phase. This method may ensure excellent dispersion and very well controlled distribution of the active species. Chemical vapour deposition is an example of gas phase deposition.

2.1.1.4. *Solid-solid reactions*

In certain cases it is possible to use a solid salt of the active element, e.g. a nitrate, to impregnate the support. This is done by dry mixing. The method is well adapted to industrial production but is difficult to use reproducibly in a laboratory.

2.1.1.5. *Wash coat*

Monolith (or honey comb) catalysts are prepared by covering the surface of the channels with a suspension of small particles in water (the suspension is called "slurry" or "slip"). Water is evaporated and the final calcination promotes adhesion of the particles to the monolith.

2.1.2. Precipitation and co-precipitation

In all precipitations it is essential to carefully control all the details of the process including:

* the order and rate of addition of one solution into the other;
* the mixing procedure;
* the pH and variation of pH during the process
* the maturation process.

Precipitation involves two distinct processes, namely nucleation and growth. Nucleation requires that the system is far from equilibrium (high supersaturation, or, in the case of ionic species, a solubility product far exceeding the solubility constant of the solid to be precipitated). Growth of the new phase takes place in conditions which gradually approach the equilibrium state.

In the co-precipitation of a phase associating two (or several) elements, if one of them is contained in an anion and the second in a cation, the precipitate will have a fixed or at least very inflexible composition. If both are cations (or both anions) the characteristics of the reactions with a common anion (or cation) of the solution, the solubility constants, and the supersaturation values will all be different, and the properties of the precipitate will change with time. Consequently, co-precipitation does not in general give homogeneous precipitates. Methods are available to produce homogeneous precipitates (see 2.1.3.).

The dispersion of the precipitate changes with the degree of supersaturation and its evolution during precipitation. Low supersaturation leads to poorly dispersed solids. Highly dispersed solids are thermodynamically unstable and tend to lose dispersion (Ostwald ripening). This takes place during the process of precipitation itself. If the effect is desired, a special maturation (or ageing) step is carried out at the end of the precipitation.

Many procedures are used for precipitation and co-precipitation. One simple method is to add drop-wise the solution containing the active component to the precipitating solution, or vice versa. There is little difference between those inverse procedures. In both cases high supersaturation can be produced locally, leading, if the solubility constant is low, to fine precipitates. If not, redissolution takes place at the beginning of the process, when agitation disperses the precipitate in the liquid. In both cases, concentrations change continuously throughout the precipitation process resulting in an inhomogeneous product being formed, at least with respect to texture. Any precipitation process is situated somewhere between two extremes. Either the solutions are contacted instantaneously (only an ideal situation as, in all cases, diffusion has to take place), the supersaturation decreasing continuously, or the supersaturation is maintained constant during the whole precipitation process.

Instantaneous precipitation is achieved by two methods. The first consists in pouring continuously, in constant proportion, both solutions into a vessel under constant and vigorous stirring. The second consists in mixing the solutions through specially designed mixing nozzles. The latter method ensures a better uniformity in composition and texture of the precipitate.

Precipitation under constant conditions is achieved in the "homogeneous precipitation" method, in which the precipitating agent (e.g. NH_4^+) is continuously supplied or produced in situ (e.g. by decomposition of urea). This method provides a low level of supersaturation, and hence, leads to poorly dispersed solids (see also 2.1.2.2.).

2.1.2.1. *Synthesis of zeolites and related materials*

The nature of the microporous frameworks of zeolites obtained by crystallisation of Al and Si containing reaction mixtures is defined by both the preparation conditions and their final structural Al content, whereas the nature and concentration of the active sites depends also on subsequent pretreatments (calcination, steaming, ion-exchange, etc.).

Zeolites are normally prepared by crystallisation (precipitation) in hydrothermal conditions (T = 350-525 K) of (Si,Al)-containing hydrogels [3]. Above 373 K, crystallisation is normally performed under autogeneous pressure. Both batch and continuous synthesis methods can be envisaged. Variables which affect the synthesis of zeolites fall into 3 categories:

* parameters which determine the *crystalline field*: reactant composition, basicity (hydroxyl content), added salts and ions (organic and/or inorganic), temperature and pressure. Of particular importance in controlling synthesis are the molar ratios (OH^-/SiO_2 and Si/Al), and temperature, which affect the solubility of (alumino)silicate species and the kinetics of non-microporous phase(s) formation [3].

* *directing effects* from the presence of structure-directing (templating) agents (organic compounds and bases, alkali cations, and other miscellaneous organic molecules). Attention should be paid to possible competition between these agents as well as to (partial) secondary reactions or degradation of the organic additives.

* miscellaneous *operational variables* the importance of which may be overlooked, such as the nature of the Si and Al sources (type of alumina and silica affecting their solubility, content and nature of contaminants, secondary reactions when using organo-Al or -Si reagents), the order of addition of the reactants (which can affect the aluminosilicate gel formation, its homogeneity, and its sorptive and templating properties), ageing and ripening prior to crystallisation (affecting gel pH, viscosity, and composition), stirring rate (mass homogeneity, uniform temperature control), presence of seed crystals (from non-intentional autoclave contamination), and synthesis time (possibility of formation of other denser non-zeolitic or zeolitic phases at long crystallisation times).

2.1.2.2. *Precipitation-deposition*

Precipitation-deposition is a special technique in which an active element (e.g. Ni) is deposited onto a carrier (e.g. SiO_2) in suspension in the precipitating solution (e.g. $Ni(NO_3)_2$) by slow addition, or *in situ* formation, of a precipitating agent (e.g. NH_4^+). The technique takes advantage of the fact that precipitation onto the carrier needs a lower supersaturation than formation of the new phase directly from the liquid. It is essential to maintain supersaturation at a constant moderate level. This is achieved, as in the homogeneous precipitation technique, by decomposition of a suitable substance (e.g. urea), which releases the precipitating agent continuously, or by controlled and progressive addition of the precipitating agent.

The technique is excellent if the primary particles of the carrier are not porous (e.g. Aerosil). With a porous support deposition takes place preferentially in the external parts.

2.1.3. Gel formation and related processes

A series of widely different techniques is considered here which, starting from solutions, give gels or solid-like substances, which retain all the active elements contained in the starting solutions, and from which the solvent

and reaction by-products are eliminated by evaporation or sublimation [4-6]. These gels are later decomposed or further transformed, usually to oxides.

The gel can be obtained by a range of different methods:

* chemical reaction, e.g. formation of a tridimensional polymer by alkoxide hydrolysis (sol-gel process) and, more generally, by polymerisation (of an anion, such as molybdate);
* complexation, e.g. with an acid-alcohol such as citric acid [7];
* freeze drying;
* addition of a gum or a gelling agent (hydroxymethyl cellulose, etc.)

Gel formation under the influence of heat and evaporation in the 'oil-drop' process is related to this group of preparation methods.

The basic principle underlying these processes is to maintain together, without segregation, all the active components present in a homogeneous solution. Once a gel or a solid-like substance is formed segregation becomes difficult, because diffusion is strongly restricted. The success of the fabrication rests on rapid transformation of the starting solution to a very viscous medium and the solid-like substance.

2.1.4. Selective removal

Selective removal is a method used for very few, but important catalysts. Raney Ni is a representative of this group. Starting from a relatively coarse powder of an alloy (e.g. $NiAl_x$, constituted of several phases in the present practice), one component (Al) is removed by a leaching agent (NaOH) leaving the active agent (Ni) in a relatively highly dispersed form.

2.1.5. Pillared layer compounds

One can take advantage of existing layered structures for making solids with approximately slit-shaped pores. Such solids are most often prepared from clays (pillared-clays). In a first step, the sign and number of the charges compensating those of the layers must be adjusted. This is generally done by Na ionic exchange. The interlayer ions are then substituted by poly-ions resulting from a condensation of ions in the solution in which the layered solid is suspended. A classical example is the Al_{13} Keggin cation: $(Al_{13}O_4(OH)_{24}(H_2O)_{12})^{7+}$. This is a critical step. Attachment of the polyions on the outer surface of the layered crystallites, as well as further polymerisation of the polyions, should be prevented. A second, equally critical step, is the removal of the interlamellar solution by careful drying or sometimes freeze drying, and progressive heating (see 2.2 below). During heating, the polyions lose their solvation water as well as the hydroxyls they may contain and bind to the layers. Pore openings may be very broad in the direction perpendicular to the layers: 1.2 to about 2 nanometers. They mainly depend on the nature of the polycation intercalated. The lateral distance between the pillars can only be controlled to a certain extent.

Successful preparation of pillared structures demands that (i) adsorption of polyions on the outside of the crystallites be prevented, (ii) polymerisation be inhibited (iii) and an attachment of the layers to basal planes or to other layers be prevented. Phenomena (i) and (ii) lead to structures with no pillars, or uncompletely pillared, and to blocking of pore mouths. Phenomenon (iii) is responsible for so-called "house of cards" structure with very large irregular mesopores.

2.2. Treatment of intermediate solids or precursors

These treatments include drying, thermal decomposition of the salts, calcination, etc. The product obtained is a reasonably inert solid (usually an oxide) which can be stored easily.

Many recommendations are common to all treatments (as well as to activation, examined below). The main recommendation is that in all these processes all the particles of catalyst be subjected statistically to exactly the same succession of conditions. A fixed bed does not ensure this uniformity. Only moving beds (fluid beds, rotating furnaces, circulating beds or spray-drying) fulfil the above requirements.

A second recommendation is to supply a sufficient quantity of gas or liquid to the reactor to ensure complete reaction (dry air or nitrogen for complete evaporation, air or oxygen for quantitative formation of oxides, etc.). In this respect special consideration should be given to mass and heat transfer. Drying may result in a loss of uniformity in the distribution of a given element in the catalyst. This occurs if the compound in which this element is contained is not sufficiently strongly attached to the solid (carrier). It can then be expelled from the pores if bubbles form in the pores, and expand. A similar effect results if migration in a liquid film occurs towards places (external surface) where evaporation takes place. Very slow drying avoids these problems. Marked improvement is often achieved by the application of freeze drying.

Salts giving gaseous decomposition products (e.g., nitrates) do not usually cause problems. With organic salts a problem may arise because of the possible formation of carbonaceous residues. Sufficient air or oxygen must be supplied to avoid this difficulty.

The same recommendations are valid for all types of calcination treatment.

All zeolites need to be thermally pretreated prior to their use as catalysts in order to remove the sorbed water. General information on this subject is available. Zeolites normally have a remarkable thermal stability (up to 875 K or more). The latter however decreases with increasing Al content and for larger pore size materials. In addition, for materials prepared in the presence of an organic agent, a calcination step is needed to remove the occluded organic species.

In both cases, framework Al may be exposed to water vapour at rather high temperature (525-875 K), which can lead to dealumination of the zeolite structure (production of non-framework Al species and decrease in the concentration of acid sites, modification of sorptive properties and catalytic behaviour). In order to avoid unwanted dealumination by minimizing the local and instantaneous water vapour pressure:

* shallow bed thermal treatments should be preferred to deep bed calcinations;
* oxidative calcination of organic-containing materials should be performed in conditions minimizing the water vapour production;
* the exposure to steam of the hydrogen forms of zeolites should be avoided as much as possible.

2.3. Activation of the precursor

In the activation of the precursor the procedures differ greatly from case to case. The recommendations under 1.1 are valid in the present case. Catalysts always contain species with different reactivities, even when of simple composition. Differences may arise from (i) different locations in the depth of the pellets (effect of diffusion on reactivity), (ii) different crystallite sizes (especially if a nucleation and growth mechanism operates),

(iii) various degrees of interaction with the support, and (iv) differences in the degree of contamination. For those reasons, the activation rate becomes slow as the degree of reaction proceeds; there are even cases where reaction is never complete. The proper characterisation of a catalyst with respect to its activation therefore requires that all the above recommendations are taken into account and that the degree of activation is carefully determined. This implies that the activated solid is carefully analysed.

If a nucleation and growth mechanism operates it is probably possible to control dispersion by modifying the rate of nucleation compared with the rate of growth. In all cases there is usually a coupling between activation and loss of dispersion. For those reasons a complicated activation procedure has to be selected in many cases. Either the composition of the activating agent or the temperature or both are changed progressively or step-wise.

Active catalytic forms of zeolites can be obtained conventionally by cation-exchange. Care should be taken to avoid chemical modifications induced by a too low or too high pH of the exchange solution, which can lead to the extraction of Al and/or Si species and the formation of lattice defects. Protonic (Brönsted) sites are generated by ammonium-exchange (preferably at buffered and slightly basic pH, 7-9) followed by calcination at 300-500°C. Higher deammoniation temperatures are preferred for materials with lower Al content (higher acidic strength). Metals can be introduced into zeolites via ion-exchange and subsequent reduction or via sorption of neutral soluble or volatile species (for example carbonyls).

2.4. Forming methods

In principle the support, precursory solids, precursors or catalysts, can be used as such (e.g. powders obtained by spray drying). But, generally the catalysts are used as entities of larger size and/or better defined shapes (beads, pellets, extrudates, rings, monoliths, etc.). Some forming operation [8] has thus to take place sometimes during preparation. This is done on the support if the deposition method (including precipitation-deposition) is used. Otherwise, a precipitate, or an intermediary solid (precursor produced by, e.g., the methods described under 2.1.1), is the material used for the forming operation. As a rule, mesoporosity (pore diameter less than 50 nm) is created before forming. The forming operations determine the porosity corresponding to larger pores.

The forming operations also determine other very important characteristics of catalysts:

* mechanical properties;
* resistance to thermal shock;
* gas or liquid flow through the reactor.

Depending on the technology (e.g. fluidisation, moving bed or fixed bed) and the conditions of the catalytic process, the shape and size of catalyst entities may vary appreciably, e.g. finely powdered, cylinders, beads, etc. A general problem is to make entities of dimensions larger than 1 mm from fine powder particles.

The powder may be either dry or slightly damp during shaping. Materials which are difficult to shape are treated with additives.

The development of zeolite-containing catalysts has led to the development of binders. Modern catalyst technology (especially for fluidized bed catalytic cracking and hydrocracking) selects binders which may have a variety of properties of their own (catalytic, trapping of poisons, etc.)

Shaping additives may act as lubricants, plasticisers, cements, porosity promoters (porogenic additives), etc. [9]. The powdered starting material mixed with the additives may be dry, or converted to a plastic pulp by the

addition of a suitable liquid. One sometimes distinguishes:

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

2.4.1. Powder: preparation, crushing and grinding

Grinding may be an essential preliminary operation, and is used sometimes for producing special commercial catalysts. In a powder, which is a collection of particles of relatively small size (typically 0.5 μm - 1mm), the particles may have different shapes and this influences strongly the shaping operations. The crushing and/or grinding operation is aimed at producing particles of a size such that after the forming operation pores of the desired size are formed. Crushing and/or grinding is used with material of natural origin or with products of operations of the 2.1.3. category. Grinding may take place in the absence (dry) or presence (wet) of a liquid, usually water.

2.4.2. Forming by crushing

This is a very special, but important, case of a forming operation used to make ammonia catalysts. The fused mass is crushed to irregular lumps and sieved to proper size [10].

2.4.3. Spray drying

In spray drying, a slurry of a powder in suspension in water is fed to a nozzle which sprays small droplets into hot air. Spray drying gives particles of almost identical shapes (spheres with a slightly depressed surface at one spot) and sizes, used as such in fluid bed operations.

2.4.4. Oil drop

A sol or gel is introduced as drops through a nozzle into a hot liquid. Heat removes the solvent and brings about the hardening of the gel. According to relative densities the drops may move downwards (oil drop per se) or upwards. Beads are obtained.

2.4.5. Granulation

Granulation (or pilling) is the agglomeration-forming operation made by progressive humidification of a powder in a rotating granulator, resulting in the formation of spheroidal particles, granules or beads. These beads are usually not very uniform in size [9]. In the operation, many differently sized individual particles are put into motion under a spray of liquid (water or aqueous solution) in a horizontal rotating cylinder or a pan rotating around an axis inclined at about 45 °. The pan may be concave (hemispheric granulator or "bowl granulator") or cylindric (flat granulator or "dish granulator").

2.4.6. Tabletting

In tabletting, the powder is firmly compressed in a die to be shaped into small cylinders, rings and even beads. In most cases some plasticising agents are added to the powder (talc, graphite, stearic acid, etc.). One may also use porosity additives (powder of an easily decomposed compound, polymer fibres, etc.). Tabletting is one of the few forming operations which has been studied systematically.

2.4.7. Extrusion

In extrusion, a paste, which may be "soft" or "stiff" (or: "wet" or "dry") is pushed through a die, forming a cylinder which is cut into small sections. Peptisation, by addition of an adequate substance, is often used before extrusion in order to induce hardening. The sections of the die may have different shapes.

Monolith is now one of the most widespread form of catalysts. Monliths are formed by extrusion through special dies creating multiple channels. (A variant in monolith manufacture uses corrugated foils of the support which are joined together to create channels).

2.5. Stability during handling and storage

The objectives of the first series of steps in the preparation of catalysts (usually corresponding to 2.1.1. and 2.1.2.) is to make a catalyst precursor, very often an oxide, the stability of which is compatible with handling and transportation. However, there is presently a trend towards carrying out activation in the manufacturing or other specialised plants so that solids more reactive chemically and more fragile mechanically have to be handled.

The solids to be stored have high surface areas and are highly reactive and sensitive to contamination. They should be stored in hermetically closed containers. All contaminants are potentially harmful:

* water; water brings about hydrolysis and formation of liquid films which dissolve active elements, and may bring about the corrosion of containers;
* CO_2; CO_2 brings about carbonate formation. The reaction of carbonates, during activation, may give an activated catalyst with altered texture;
* hydrocarbons; if hydrocarbons are present, there is a danger of uncontrolled reactions during calcination (overheating) or activation (over-reduction);
* poisons.

2.5.1. Activated catalysts

Practically all cases where protection of activated catalysts is necessary correspond to metal or reduced-sulfided catalysts. Three methods are widely used for protecting these catalysts from alteration during storage and handling.

2.5.1.1. *Passivation*

Passivation often involves the controlled exposure of the catalyst to air at ambient temperature. Rapid exothermic reactions are prevented while forming stable surface layers which inhibit further rapid reaction upon air exposure. Similar exposure to other passivating reagents would also lead to air stable surface layers on the metallic surfaces. A typical example is the passivation of Ni catalysts which would oxidize catastrophically upon exposure to air, and of highly dispersed supported Pt catalysts. Many methods or techniques are available: controlled oxidation, adsorption of protecting (usually inhibiting) molecules, reactions with a weakly oxidising agent dissolved in water.

2.5.1.2. Protection by an inert gas

Activated metal catalysts and hydrodesulfurisation catalysts can be stored and handled in an inert atmosphere (N_2). This can be achieved industrially without excessive cost.

2.5.1.3. Protection by a condensed phase

Activated metal catalysts (essentially Ni) can be effectively protected by a wax (stearic acid, etc.). Even catalysts in a powder form, for use as suspensions, can be protected this way. The waxy mixture is shaped to pellets. Part of the catalysts used in the fat and oil industry undergoes this treatment.

3. CHARACTERISATION OF SURFACE PROPERTIES BY ADSORPTION METHODS

Adsorption methods may be used to provide information about the total surface area of a catalyst, the surface area of the phase carrying the active sites, or possibly even the type and number of active sites. The interaction between the adsorbate and the adsorbent may be chemical (chemisorption) or physical (physisorption) in nature and ideally should be a surface-specific interaction. It is necessary to be aware, however, that in some cases the interaction between the adsorbate and the adsorbent can lead to a chemical reaction in which more than just the surface layer of the adsorbent is involved. For example, when using oxidising compounds as adsorbates (O_2 or N_2O) with metals such as copper or nickel or sulfides, sub-surface oxidation may occur.

Physical adsorption is used in the BET method to determine total surface areas and this has been described in a previous IUPAC document [11].

Many catalysts comprise an active component deposited on a support. In order to investigate relationships between catalytic properties and the amount of active surface it is necessary to have a means of determining the surface area of the phase carrying the active sites (which we shall call active phase hereafter) in the presence of the support. One has to resort to phenomena specific to the active phase. Chemisorption on the active phase is commonly used for this purpose.

Because of its intrinsically *specific* nature, chemisorption has an irreplaceable role. It should be recognised, however, that well defined thermodynamic equilibrium physisorption is much more difficult to achieve by chemisorption than with physisorption. Moreover, it does not obey simple kinetics. Empiricism permits the derivation of procedures which give reproducible results, and yield values which are proportional to the true surface area within certain limits. But the real coefficient of proportionality is actually unknown. Different procedures are used, according to the nature of the active phase/support system to be characterised, and depending on the choice of adsorbate. Provided standard, reproducible procedures are used, invaluable information can be obtained.

A wide variety of adsorbates has been used, the choice depending on the nature of the surface to be examined and the type of information being pursued; e.g. for metals, H_2, CO, O_2 and N_2O; for sulfides, NO, CO, O_2, H_2S and organo-sulfur compounds; for oxides, NH_3, CO_2 and various organic compounds.

With simple probe molecules, such as H_2, information about the number of surface metal atoms is readily obtained by using adsorption measurements. However, even with such simple probe molecules further information about the heterogeneity of a surface may be obtained by performing temperature-programmed desorption measurements. With probe molecules which are chemically more specific (e.g., NH_3 and organic amines, H_2S and organic sulfides) it may be possible to obtain information about the number and nature of

specific types of surface sites, for example, the number and strength of Lewis or Bronsted acid sites on oxides, zeolites or sulfides.

The use of more than one technique can provide important additional information about the nature of sites on a particular solid surface. For example, infrared spectroscopy may be used in conjunction with quantitative chemisorption measurements of CO to determine the type of binding of CO and hence the nature and number of the active sites. The combination of chemisorption and ESR spectroscopy permits the characterisation of the electronic properties of the surface.

Care should be taken when using adsorption with microporous solids, as new effets may arise. Specific literature should be consulted in this case.

3.1. Methodology

Adsorption can be performed in a number of different ways which may involve static and flow or dynamic techniques.

3.1.1. Static methods

The static methods are volumetric or gravimetric. The volumetric method involves the use of a vacuum system comprising two sections, a dosing section which allows the introduction of accurately measured quantities of the adsorbate, and a sample section which contains the catalyst. The precision of the volumetric method depends on accurate calibrations of volumes, including the dead space in the sample section, precise control of the temperature of the dosing and sample sections, and accurate pressure measurement.

Gravimetric methods may be used to determine adsorption of most molecules, even H_2 if proper instruments are used. An advantage of the gravimetric method is that it eliminates the requirement to make dead volume corrections. Also, in contrast to the volumetric method, this technique does not lead to cumulative errors since the quantity of gas adsorbed and the equilibrium pressure are measured independently of each other. The main disadvantages are the high sensitivity to weight changes required, the difficulty in controlling the temperature of the sample, and taking account of buoyancy corrections, particularly in flow experiments.

3.1.2. Dynamic methods

In the single flow technique, a carrier gas containing the molecules to be adsorbed pass continuously over the catalyst. The flow method of determining gas adsorption has the advantages that no vacuum system is required and no dead volume corrections need to be made. The method is also rapid and easy to use. Disadvantages are the need to use very pure carrier gases, and the fact that for slow or activated adsorption processes equilibrium adsorption may be difficult to determine. The flow method is not recommended for obtaining total isotherms.

The pulse technique is in many ways similar to the flow technique except that the adsorbate is introduced by adding pulses (e.g. from a gas sample valve) into the carrier gas. The pulse volume is chosen so that the first few pulses will be completely adsorbed. Further pulses are introduced until no more gas is adsorbed. The quantity of gas adsorbed is calculated by summing up the amounts adsorbed in the successive pulses. This technique is only applicable for strongly retained adsorbates.

Chromatographic methods are widely used for the study of both physisorption and chemisorption. In its simplest form the technique consists of passing a pulse of the adsorbate through a column of the adsorbent and measuring the retention time and registering the elution curve. Measurement of the variation in the retention time as a function of temperature permits the evaluation of the enthalpy of adsorption, and analysis of the shape of the elution curve provides information about the adsorption isotherm.

It is possible to determine the amount adsorbed by a titration method. For example, the amount of hydrogen adsorbed on a Pt surface may be titrated with pulses of oxygen. The oxygen adsorbed can in turn be further titrated by pulses of hydrogen. From the stoichiometry of the H_2/O_2 reaction a measure of the number of surface metal atoms can be obtained.

3.1.3. Desorption

Desorption is always an activated process and may conveniently be studied by temperature-programming techniques. Information is obtained in this way on the adsorption kinetics and the energetics of the gas/solid interactions.

3.1.4. Precautions

The choice of experimental conditions for the adsorption experiment is critical and must be based on experimentation for each active phase of interest. Since the amount of surface area of the active phase depends on the method of pretreatment, a standardised pretreatment of the material before chemisorption is essential. For example, this involves using conditions of flow rate of gas, heating rate, time of heating, final temperature, etc., identical to those used in any other related study of the same catalytic material.

Problems in the determination of the surface area of active phases can arise from a number of sources. An overestimation of the amount of active surface can be caused by spillover of the adsorbing species on the support, solubility in the adsorbent, subsurface oxidation (when using O_2 or N_2O), or as a result of additional physical adsorption on the support. The extent to which these factors affect the accuracy of the results depends on the nature of the active phase, the support, and the conditions of the experiment. Problems can occur with adsorptives which may "corrode" the surface. For example, CO can remove Ni atoms from the surface of small Ni particles even at ambient temperatures.

Further problems can arise because of uncertainties concerning the stoichiometry of the adsorption reaction. For most metals it is assumed that the surface stoichiometry with H_2 is H/M = 1. However, there is evidence especially for very small metal particles (of the order of 1-5 nm) that the stoichiometry can exceed H/M = 1. For quantitative measurements of surface area it is necessary to establish the chemisorption stoichiometry and structure. In practice it is usually possible to achieve approximate estimate of the surface area by some other independent method (for example, from particle size analysis by X-ray line broadening or by TEM). In the case of CO, the CO/M ratio is generally taken as 1.0, but the true value may depend on the particle size and on the particle morphology. With N_2O the N_2O/M ratio at monolayer coverage is usually assumed to be 0.5, but once again there is no certainty about the validity of this particular assumption.

This problem of the stoichiometry of the surface reaction is a general one and is probably best circumvented

by reporting the adsorption data as the amount of adsorbed gas per unit mass of the catalyst or of the active phase under well defined conditions.

3.2. Categories of catalysts

The choice of adsorbate and the methodology depends on the nature of the adsorbent. In principle, the following categories should be distinguished as follows

(a) metals;

(b) zeolites;

(c) other acidic oxides, especially amorphous and poorly crystalline ones;

(d) other oxides, of which oxidation multicomponent catalysts constitute an important subcategory;

(e) sulfides (hydrotreating catalysts);

(f) carbides, nitrides and other solids.

The following sections will consider only categories (a), (b) and (c), and (e). In spite of the importance of category (d), no general guidelines emerge. Category (f) corresponds to catalysts still in primary stages of evaluations. We shall not examine the use of chemisorption for these categories.

3.2.1. Metals [12-16]

The first step in a chemisorption measurement on a metal is reduction in hydrogen except in cases where preparation ensures perfect cleanliness. The temperature and time of reduction are determined by the metal involved, higher temperatures being required for Fe, Co and Ni, for example, than for Pt group metals. After reduction, the hydrogen is removed from the surface of the metal by evacuation or by flushing with a very pure inert gas (He or Ar is preferred because N_2 may react with some metals to form nitrides). The desorption temperature is usually chosen to be about 20-50 ^{o}C lower than the reduction temperature. Desorption of hydrogen is continued at this temperature, typically for 0.5-1.0 h, at which point the sample is cooled to the temperature of the chemisorption experiment. Too low a temperature can cause problems due to an increase in the amount of physical adsorption on the support, or because of long delays in attaining equilibrium; too high a temperature can cause problems due to restructuration of surfaces, migration of impurities from bulk or support or because of a decrease in the amount of absorbate on the active surface due to non-adsorption into weakly binding surface sites.

An important parameter is the time allowed for the adsorption steps. In principle, adsorption on a clean metal surface should be very rapid at ambient temperature. However, in practice, particularly with metals such as Fe, Co or Ni, there is often a substantial contribution from a slow adsorption process. An arbitrary time for approximate equilibration is normally determined by experimentation, e.g., by ascertaining the time after which the pressure in a volumetric system decreases at a rate less than a preset value. Typical adsorption times for Pt metals range from a few minutes up to about 1 h, while for Ni equilibration times generally need to be in excess of 1 h, and often as long as 16 h is required for the first adsorption point. After measurement at the first equilibrium pressure further doses of adsorbate are introduced and the adsorption repeated. The time required to attain approximate equilibrium for the second and subsequent points is less than for the first, typically a few minutes for Pt metals and 1 h for Ni. By measuring a second isotherm after evacuation, the total and irreversibly adsorbed amounts of hydrogen can in principle be distinguished.

Ideally, true adsorption equilibrium should be measured. To prove that, the amount adsorbed should be the same when reaching equilibrium from lower and higher pressures (or temperatures). If not, this is the proof that processes other than adsorption take place.

The pressure range used for the determination of the adsorption isotherm depends on the nature of the metal and on the choice of adsorbate. For example, with hydrogen on Ni the pressure range is usually from about 10 kPa to about 50 kPa, whereas for Pt, pressures an order of magnitude lower may be used.

Several methods are used to calculate the amount of adsorbate corresponding to monolayer coverage. Extrapolation of the nearly linear high pressure portion of the adsorption isotherm back to zero pressure, and calculation of the amount of gas adsorbed at zero pressure is the most usual procedure. One reason for chosing this method is that it minimises errors due to weak adsorption on the support since at low pressures this is directly proportional to the adsorption pressure. An alternative means of determining the monolayer coverage is to measure the quantity of gas adsorbed at a fixed reference pressure (e.g., about 25 kPa).

In the particular case of Ni catalysts, where adsorption is slow, the reverse, or desorption, isotherm method has been devised. The first measurement is made at a high pressure of hydrogen (typically about 50 kPa) after about 45 minutes. Although hydrogen is still being adsorbed it is assumed that the values measured represents a good compromise: the amount of hydrogen still needed to reach equilibrium and the increasing amount of hydrogen adsorbed by the support due to spillover are supposed to cancel out. After this first measurement, a desorption isotherm is determined by progressively removing hydrogen from the system. Extrapolation of the desorption isotherm back to zero pressure provides a means of determining the monolayer coverage. It is generally observed that the desorption isotherm has a lower slope than the corresponding adsorption isotherm.

To measure hydrogen adsorption using the flow method a sample previously reduced and flushed free of hydrogen by an inert gas stream (usually Ar) is exposed to a constant flow of, for example, a H_2/Ar mixture (typically containing 2% H_2) and the quantity of hydrogen adsorbed is determined, often using a thermal conductivity detector. The quantity of hydrogen adsorbed corresponds to the equilibrium adsorption at the partial pressure of hydrogen used in the experiment (for example, 2% of atmospheric pressure). This is taken to be a measure of the monolayer coverage by H_2.

The use of N_2O to determine Cu surface areas requires great care to avoid sub-surface oxidation. The frontal chromatography method, in which a dilute mixture of N_2O and He (typically, 2% N_2O) is passed over a large bed of catalyst until no further N_2O is reacted, appears to be the most reliable method. In the pulse method the extent of sub-surface oxidation depends on the temperature (a very serious problem above about 100 °C), the size of the N_2O pulse, the size of the catalyst sample, the metal loading of the sample, and the geometry of the catalyst bed. In general, small pulses of N_2O should be used, at temperatures below about 60 °C, with a deep catalyst bed (>1 cm).

3.2.2. Acidic amorphous oxides and zeolites

A description of catalyst acidity requires the determination of the nature, number and strength of acid sites [17-19]. The Brönsted acid sites are able to transfer a proton from the solid to a suitable adsorbed molecule; the Lewis acid sites are able to accept an electron pair from a suitable adsorbed molecule. A particular acidic solid usually does not contain only a single class of acidic sites. Both Brönsted and Lewis sites may be present.

Moreover, in general, there will be a distribution of strengths of acid sites. The acidity of a surface may be determined using aqueous or nonaqueous methods. When aqueous methods are used, some complications may arise because water may alter the structure of the solid, equalize acidity strengths, or create new sites, for example transformation of Lewis sites into Brönsted sites.

Aqueous methods include the use of ion exchange to determine the total number of acid sites, and titration of aqueous slurries of the acidic solids with a standard base. The method cannot be applied to water-sensitive solids.

Nonaqueous methods include the use of amine titration and adsorption of indicators for visual measurement of acid strength. This procedure allows both the determination of the total amount of acid sites and also the acid strength distribution. A disadvantage is that bulky molecules (amines and indicators) are used and these may be excluded from entering small pores. With zeolites, the slow rate of diffusion and equilibration has to be taken into account. Spectroscopic measurement of acid strength may also be performed using amine titration and indicator adsorption. Ultraviolet or fluorescent indicators may be used.

Microcalorimetric measurements during adsorption of suitable probe molecules and temperature-programmed desorption of chemisorbed bases are important methods of studying acidity. The equipment required is simple to construct and operate, for example a temperature-programmable flow microreactor coupled to a thermal conductivity-type detector. When the temperature is increased linearly, the rate of desorption of an adsorbed base (for example, ammonia, organic amine, pyridine, etc.) will show a maximum in temperature, and under ideal conditions, this may be related to the activation energy of desorption. By varying the degree of coverage of the acidic oxide with the base, it may be possible to obtain a broad spectrum of strengths of adsorption as a function of surface coverage. A variation on this method is to determine the adsorption of a weak base at different degrees of pre-poisoning with a strong base.

Infrared spectroscopy is an important technique for studying acidity. Acidic OH groups can be studied directly. Probe molecules such as pyridine may be used to study both Brönsted and Lewis acidity since two forms of adsorbed probes are easily distinguished by their infrared spectra. Quantitative infrared spectroscopy may be performed by measuring the spectrum of acidic OH or probes adsorbed on thin, self-supporting wafers of the acidic solid. Other spectroscopic methods which may provide information in specific cases include Fourier Transform Raman spectroscopy, electron spin resonance spectroscopy, ultraviolet spectroscopy, and nuclear magnetic resonance spectroscopy.

Finally, it may be possible to use the rate of a chemical reaction to determine the actual number of active acidic sites. Furthermore, it may be possible to obtain an estimate of the range of strengths of acid sites by using different reactant molecules. For example, it is known that dehydration of alcohols requires only relatively weak acid sites, whereas cracking of alkanes requires very strong acid sites.

3.2.3. Sulfides

The problem with sulfide catalysts (hydrotreatment) is to determine the active centres, which represent only part of their total surface area. Chemisorption of O_2, CO and NO is used, and some attempts concern NH_3, pyridine and thiophene. Static volumetric methods or dynamic methods (pulse or frontal mode) may be used, but the techniques do not seem yet reliable, due to the possible modification (oxidation) of the surface or subsurface regions by O_2 or NO probe molecules or the kinetics of adsorption. CO might be more promising. Infrared

spectroscopy, especially FTIR seems necessary to characterise co-ordinatively unsaturated sites, which are essential for catalytic activity. CO and NO can also be used to identify the chemical nature of sites (sulfided, partially reduced or reduced sites). For such measurements, the samples must be sulfided or resulfided in the IR cell. The technique still needs improvements and standardisation.

4. FINE STRUCTURE OF CATALYSTS [20]

4.1. Surface structure and chemical composition

Although many techniques are available for the examination of solids not all are appropriate for the study of real catalysts and some require special expertise in the interpretation of the results. Moreover, the nature of the sample may be changed by the application of the technique. Therefore, it is essential to chose appropriate techniques very carefully and to be aware of the problems associated with each specific method.

Heterogeneous catalysis being concerned with surfaces, it is recommended in principle that surface sensitive methods should be used. However, some surface sensitive techniques are only sensitive to the peripheral zones of particles and cannot probe the internal surfaces of porous materials. These techniques, therefore, find limited application in the study of porous catalysts. Access to these inner surfaces is gained by using other techniques where the incident probe and the returning signal are both penetrating. (The following sections concentrate on methods in this category.)

The fact that surface atoms in the system may make only a small contribution to the total signal is a potential problem but it is minimised in the important case of highly dispersed metal particles within the pores of high area supports. Small particle sizes ensure that the major fraction of the detected signal is generated by surface atoms. A large number of particles within the volume sampled ensures adequate signal strength.

4.2. Surface structure and topography

4.2.1. Electron microscopy

In electron microscopy as in any field of optics the overall contrast is due to differential absorption of photons or particles (amplitude contrast) or diffraction phenomena (phase contrast). The method provides identification of phases and structural information on crystals, direct images of surfaces and elemental composition and distribution (see section 4.9). Routine applications, however, may be hampered by complexities of image interpretation and by constraints on the type and preparation of specimens and on the environment within the microscope.

4.2.1.1. *Conventional transmission electron microscopy (CTEM)*

It is advisable to use CTEM rather than TEM (transmission electron microscopy) to designate the method (TEM may cover several techniques). CTEM takes advantage of amplitude contrast (Bright field imaging mode). CTEM is suitable for examination of supported catalysts with particle sizes down to 2-3 nm, giving information on particle location over the support, on particle-size distributions in favourable cases, on particle and support morphology and on the nature and distribution of deposits having a thickness of the order of 2-3 nm. Surface topography can be examined using replication techniques. For particles smaller than about 2 nm analysis of micrographs on a routine basis is not possible and even in the 2-10 nm range interpretation must be approached with caution.

4.2.1.2. *Techniques related to CTEM*

4.2.1.2.A. Dark field methods

Dark field images are obtained by admitting only diffracted electrons and excluding directly transmitted electrons. Dark field imaging selectively detects crystallites with crystallographic plane spacings within a relatively narrow range.

4.2.1.2.B. High resolution electron microscopy (HREM)

The periodic structure of a crystal is not visible in a CTEM image but is revealed, to a limited extent, if the technique is converted to HREM by modifying the method of image formation either in the CTEM instrument or in specialised machines operating at 0.5-1.0 MeV. Lattice Fringe images represent the simplest case and show an intensity modulation which gives the spacing of the atomic planes lying parallel to the incident beam, enabling catalyst particles to be identified. In certain instances fringes from the support can be used for an accurate assessment of small (down to 1 nm) particle sizes, and to determine pore dimensions and interlayer distances. In the case of heavy metals the crystal structure of particles of this size can be studied also. The amount of crystallographic information is increased by the formation of Structure Images but interpretation then requires comparison with images reconstructed by computer.

4.2.1.2.C. Reflection electron microscopy (REM) and reflection high energy electron diffraction (RHEED)

When the specimen is set at a glancing (or grazing) angle to the incident beam, images of the surface may be obtained together with RHEED patterns; (the RHEED experiment can also be carried out in a dedicated instrument). The method is sensitive to atomic-height features such as steps, emergent dislocations and small particles on smooth surfaces.

4.2.1.2.D. Scanning electron microscopy (SEM) [21]

Topographical images in a SEM are formed from back-scattered primary or low-energy secondary electrons. The best resolution is about 2-5 nm but many routine studies are satisfied with a lower value and exploit the ease of image interpretation and the extrordinary depth of field to obtain a comprehensive view of the specimen. With non-crystalline catalysts, SEM is especially useful for examining the distribution and sizes of mesopores. An energy dispersive X-ray spectroscopy device is a frequent attachment in the instrument (see section 4.9).

4.2.1.2.E. Scanning transmission electron microscopy (STEM) [22]

STEM represents a merger of the concepts of TEM and SEM. Modes of operation and mechanisms of contrast and of imaging are essentially the same as in CTEM but the main advantage of STEM is the ability to carry out microanalysis at very high resolution (see section 4.9).

4.2.1.2.F. Selected area diffraction (also called: microdiffraction)

In both CTEM and STEM, diffraction patterns can be recorded from small areas of the specimen by positioning the beam at a chosen point in the image and switching to diffraction mode. Because CTEM uses a non-convergent (parallel) beam, the minimum region which can be sampled is about 500 nm and the selected

area diffraction patterns obtained are of the usual electron diffraction type, giving two-dimensional interplanar spacings and angles. In STEM the incident beam is convergent and areas from 50 nm (microdiffraction) down to less than 1 nm (nanodiffraction) (the latter in dedicated instruments) can be examined. In addition, the region of reciprocal space sampled in convergent beam diffraction is larger than in the case of selected area diffraction. Hence, a *single* convergent beam diffraction pattern can provide very accurate three-dimensional crystal symmetry information, allowing a full analysis of the point and/or space group of the material. In comparison with XRD, the volume examined is minute.

4.3. X-ray and neutron methods for structure determination

4.3.1. X-ray diffraction and diffusion

X-ray diffraction (XRD, sometimes also called WAXS: wide-angle X-ray scattering) is one of the most important techniques for catalyst characterization. For most catalysts XRD is limited to powder-pattern identification of crystalline phases. For zeolites, and catalysts with good crystallinity, long range order exists, and XRD can give a complete description of their structure. In all cases, the possible presence of amorphous phases should be taken into account in interpretation.

The technique can be complemented by line-broadening analysis which gives valuable information on the size of individual crystallites. Variations of ratios between lines indicate either order imperfections along certain crystallographic directions or spontaneous orientation of the crystallites in the sample holder.

Small angle X-ray scattering (SAXS) provides information on ultradisperse (e.g. colloidal) and generally poorly ordered materials. The technique is very close to RED (4.3.2) in several aspects, and can, in principle, be applied in the same equipment. Commercial equipments exist; they are equipped with a rotating anode for generating high X-ray intensities. Interpretation needs a sophisticated software.

For all these equipments, attachments permit measurements at high temperatures and in controlled atmospheres.

4.3.2. Radial electron distribution (RED)

In samples with crystallites of size less than about 1.0-1.5 nm and in amorphous samples periodicity does not extend over a range sufficiently long to be detected by the XRD process. In practical terms the only structural information accessible concerns short-range order. Analysis of the X-ray wide-angle scattered intensity gives interatomic distances and co-ordination numbers, averaged spherically around all atoms. Excellent information can be obtained with solids composed of one single or two different atoms. Good information can be obtained if one type of atom in a more complex solid has a sufficient concentration and an atomic weight much larger than the others: the information then concerns that particular atom. For supported metals, estimates of structures, morphology and size may also be obtained if the atomic number of the metal is much larger than that of the atoms constituting the support.

4.3.3. Extended X-ray absorption fine structure (EXAFS) [20]

The oscillations which occur in the X-ray absorption coefficient in the energy range of 50-1000 eV above an absorption edge contain information on the distances between the absorbing atom and its surrounding co-

ordination spheres, the number of surrounding atoms, the identities of the absorber and its neighbours and the dynamic and static disorder in the internuclear distances.

The distance to the first co-ordination shell can be determined to within 1-2 pm, particularly when elements of higher atomic number are involved; for succeeding shells accuracy falls to 10-20 pm. Uncertainty in co-ordination numbers is greater, being about 20% for the first shell. (The RED technique gives interatomic distances directly and accuracy does not fall sharply beyond the first shell.) The major advantage of EXAFS is that the short-range chemistry it reflects can be examined separately around each type of atom, a facility which is particularly useful for the study of multimetallic catalysts and which is not available with RED. [23,24]

4.3.4. Techniques related to EXAFS

In the X-ray absorption edge spectroscopy, enhanced absorption occurs at the L_2 and L_3 edges of certain elements giving a 'white line' with an intensity proportional to the number of d-electron vacancies in the absorbing system. Fractional differences in d-electron band occupancy can be investigated for the absorber in various environments including compounds and small catalyst particles. Characterization by surface extended X-ray absorption fine structure (SEXAFS) [25] is best achieved by monitoring the photoelectrons, Auger electrons or secondary electrons generated by X-ray absorption. These emissions relate directly to the X-ray absorption coefficient but originate within the first few atom layers at the surface. X-ray absorption fine structure (NEXAFS or XANES) [24,25] contains information on bond angles and site symmetries and thus gives valuable structural data. Data analysis, however, is more complex than in EXAFS, molecular chemisorption being the most tractable case.

EXAFS-type fine structure can also be detected in high-energy electron-energy-loss experiments either in transmission through very thin samples using an electron microscope (extended energy loss fine structure, EXELFS; see section 4.9.2) or in a surface-sensitive reflection mode (SEELFS, 'surface extended') using an Auger spectrometer [26].

4.3.5. Neutron diffraction

Neutron diffraction gives the same kind of information as X-ray diffraction. Signal strengths are low but neutrons permit specimen examination under extreme conditions of temperature and pressure and detection of low-Z elements, particularly deuterium. The method may also take advantage of differences in cross-section between pairs of catalytically important atoms which are larger than the corresponding differences in the X-ray case. Large amounts of sample are necessary (often around 1 kg). [23,27]

4.4. Ion scattering techniques

Ion scattering spectroscopy (ISS), or low-energy ion scattering (LEIS), and Rutherford backscattering spectroscopy (RBS), or nuclear backscattering spectroscopy (BNS) or high-energy ion scattering (HEIS) are well established for chemical analysis, but for structure determination they are at the development stage. ISS is now a commonly used technique. A beam of ions (usually 1-5 keV noble gas ions) is directed on the surface. Although such high energy ions can penetrate the solid, only backscattered primary ions are examined which have undergone an inelastic collision with the first atom layer at the surface and so the technique has extreme surface

sensitivity. The energy spectrum of the backscattered ions is equivalent to a mass spectrum of the surface, with a detection limit of about 0.1 monolayer. Given suitable pretreatment and calibration procedures, an accuracy of 5-10% can be achieved in quantitative elemental analysis. The use of noble gas ions of different atomic masses permits resolution of signals coming from a wide range of different surface ions.

In RBS techniques incident protons (200-400 keV) or helium ions (1-3 MeV) are used with a penetration depth of several microns. The technique is useful for examining the geometry of catalyst pores, particularly those below about 2 nm, which are not easy to study by other methods. In principle, target atom identity and position can be determined simultaneously by an energy analysis of the backscattered ions but data interpretation is not possible if more than three elements are present in the specimen. Sensitivity is greatest for heavy atoms in a light matrix and concentrations can be measured to better than 5%. Refinements are possible for single crystals, such as epitaxy, but the corresponding techniques are outside the scope of the present document.

4.5. Electron state and local environment of elements

Three techniques give access to the environment of nuclei (electronic shells, valency, symmetry, matrix interactions). All of them are bulk techniques but when properly used, are extremely useful for catalysis.

4.5.1. Nuclear magnetic resonance (NMR) (20)

The quantum energy levels of a nucleus depend on all the electric and magnetic interactions to which is is subjected. These are influenced by the nature of the bonds in which it is involved, elements present in the vicinity (a few tenths of a nanometer), and the local structure of the matrix. Compared to SAXS, RED or EXAFS, NMR gives little information on distance but much more details on the chemical environment.

Spectra of solids are complicated, because of the multiplicity of parameters involved, especially by anisotropic interactions as dipolar coupling. Many techniques both experimental or computational have been developed for interpretation. A technique particularly useful for catalysis permits to selectively suppress anisotropic contributions by mechanical rotation of the sample (magic angle spinning, MASNMR) and by rotation of the nuclear magnetic dipoles with sequences of radio-frequency pulses.

Dynamic phenomena such as surface mobility can be approached by NMR because some signals either average or not according to lifetime of configurations.

The inherent sensitivity of NMR is low. It is however possible to get larger signals from surfaces by using highly dispersed or porous materials. The easiest nucleus to study is ^{1}H while organic adsorbates can be investigated using the ^{13}C resonance. A wide variety of zeolitic solids [28-30] has been studied using ^{27}Al and ^{29}Si NMR, the chemical shifts obtained by MASNMR revealing the local structure in the vicinity of a given nucleus. ^{129}Xe NMR as a probe atom adsorbed in pores is useful for determining the pore structure of zeolites. Most transition elements have a magnetically-active isotope but adequate signals can be expected in a few cases only, including ^{51}V, ^{55}Mn, ^{59}Co, ^{93}Nb, ^{185}Re, ^{187}Re, and ^{195}Pt.

4.5.2. Electron spin resonance (ESR)

ESR permits the determination of the number and location of unpaired electrons. These data provide information concerning the structure and environment of surface species. Sensitivity is high, with the

possibility of detecting 10^{11} spins in favourable cases, namely species present at concentrations of about one part per billion, but polycrystalline samples with the paramagnetic centres randomly oriented often generate spectra which are poorly resolved. Catalytic applications include investigations: of adsorbed radicals, particularly those containing oxygen: of transition metal ions on oxide surfaces: in zeolites, as probes of the environment in the vicinity of the ion. Weak interactions can be observed by special pulsed methods, including the electron spin echo technique.

4.5.3. Mössbauer spectroscopy

Mössbauer spectra provide information on: (a) the oxidation state, co-ordination number and ligand type of the resonant atom; (b) on the electron distribution in the resonant atom and the electric charges on its neighbours; (c) on ferromagnetic ordering in iron and its alloys, which is particle size dependent; and on the strength of binding of the resonant atom to its surroundings. Mössbauer measurements at room temperature and above can be made routinely only with a limited number of isotopes, including ^{57}Fe, ^{119}Sn, ^{121}Sb, ^{151}Eu, and ^{181}Ta; The use for pure catalysts is thus limited but by doping a material with no Mössbauer activity of its own with a few percent of a Mössbauer-active species (e.g. ^{57}Fe), a spectrum is obtained which is sensitive to the nature of the host matrix immediately surrounding the dopant atoms. In such experiments, however, independent measurements must demonstrate that the Mössbauer-active material is in the sample and atomically dispersed through the matrix.

In the usual transmission mode of operation, surface sensitivity can be achieved by examining very small particles (<10 nm) or thin foils (<2.5 nm) but an alternative approach involving backscattered electrons or fluorescent X-rays is under development. [31]

For some purposes it is useful to employ the emission mode of operation, e.g., for the study of Co in sulfides. It should be checked that the cascade of nuclear and electronic events involved in emission does not generate false signals, especially when the matrix is poorly conducting. Mössbauer spectroscopy is in principle a bulk technique and its application to catalysts problems requires differentiation between bulk and surface lattice positions.

4.6. Vibrational spectroscopies

4.6.1. Transmission infrared spectroscopy (IR)

This vibrational spectroscopy is used for characterisation of high area supported or unsupported catalysts, including zeolites. Information is available, either directly or by study of 'probe' adsorbates, on the chemistry of surface groups (particularly on oxides). It is also used for the study of the behaviour of precursor compounds during catalyst preparation. Problems include low transmission at high metal loadings and strong oxide scattering. Absorption at lower wavenumbers often prevents observation of modes such as adsorbate-metal stretching.

Fourier Transform (FTIR) spectrometers offer two pronounced advantages over dispersive instruments: higher energy throughput and faster data acquisition or higher signal-to-noise ratio. Data processing is easy. These features are significant when examining very strongly absorbing and scattering solids and when following dynamic processes. Much IR transmission work, however, requires examination of only limited frequency ranges at medium resolution and computerised dispersive spectrometers may then be preferable.

Examination of infrared-opaque catalysts, e.g., carbon-supported, coked or which have high metal loadings, requires special specimen preparation techniques. These may be avoided by using other vibrational techniques described below.

4.6.2. Infrared emission spectroscopy

There are few catalytic applications of this method. Low signal strengths make the use of Fourier Transform (FT) spectrometers advantageous.

4.6.3. Diffuse reflectance spectroscopy (DRS)

DRS provides spectra in the range 200-15000 cm^{-1} and is useful for specimens which absorb and scatter IR radiation very strongly. It benefits from being used with FT spectrometer (DRIFT).

4.6.4. Internal reflectance spectroscopy

Catalysts can be examined as either very fine powders or pressed wafers but the technique has not been developed extensively.

4.6.5. Photoacoustic spectroscopy (PAS)

A PAS cell coupled to an FT spectrometer covers the uv-visible and i.r. ranges. Metals are difficult to examine and catalyst studies have been limited.

4.6.6. Others

There is a number of vibrational spectroscopic techniques not directly applicable to the study of real catalysts but which are used with model surfaces, such as single crystals. These include: reflection-absorption infrared spectroscopy (RAIRS or IRAS); high resolution electron energy loss spectroscopy (HREELS, EELS); infrared ellipsometric spectroscopy.

4.6.7. Raman spectroscopy

This technique is widely applicable. The large frequency range (50-4000 cm^{-1}) makes adsorbate-adsorbent stretching modes accessible. Problems include specimen heating, high background fluorescence and low signal strengths. Surface enhanced Raman scattering (SERS), however, can give greatly increased signals in favourable cases, e.g., with rough surfaces or small particles of certain compounds. It is particularly useful in the studies of supported monolayer catalysts and adsorbed layers.

4.6.8. Inelastic neutron scattering spectroscopy (INS)

Using incident neutrons with a continuously varying energy in the range 5-500 MeV and registering the spectra of backscattered neutrons, information can be obtained on vibrational modes in adsorbed molecules. As the cross section of the hydrogen atom is one order of magnitude larger than that of other atoms, the technique is mainly used to study the hydrogen or hydrogen-containing species adsorbed on a wide variety of substrates.

4.8. Electron spectroscopies

Electron spectroscopy was first developed for chemical analysis (ESCA). In the form of core photoelectron spectroscopy (XPES, often shortened to XPS), valence band photoelectron spectroscopy (UPES, also called PES or UPS) and Auger electron spectroscopy (AES) it can be applied on a routine basis for rapid chemical analysis of a large variety of solid surfaces; neither technique detects hydrogen nor does AES detect helium. Surface sensitivity is high, the depth sampled being in the approximate range 2-10 atom layers. A qualitative interpretation of the spectra is straightforward but quantitative interpretation can present a number of problems.

4.8.1. Photoelectron spectroscopy (XPES, UPES)

X-ray photoelectron spectroscopy (XPES) is based on the analysis of the kinetic energy distribution of core level photoelectrons ejected as the result of irradiation with monochromatic or narrow band X-rays. The best sensitivity is of the order of a few percent of a monolayer and for most instruments spatial resolution is around 0.2 mm. With suitable calibration procedures elemental surface concentrations can be measured with an accuracy of the order of 20%. It constitutes a major tool in catalyst characterization. The major interest is centred on observations of 'chemical shift' effects which reflect the oxidation state, and the chemical environment of the emitter. Quantitative applications, especially to complex systems such as catalysts, can involve problems due to sample charging and to the choice of calibration procedures. They usually necessitate independent data concerning catalyst structure and texture. XPES has been widely used in catalyst research to provide general qualitative analyses, to investigate the depth profile distribution of active species, to obtain estimates of dispersion, clustering and other morphological variations, to study metal-metal and metal-support interactions and to examine the chemical states of additives, poisons and transition metal ions in zeolites. Proven measurement techniques and models for interpretation [32-34] are available.

Ultraviolet photoelectron spectroscopy (UPES) probes the valence band in the solid or the molecular orbitals in adsorbed species. The technique has no direct analytical potential but gives information on the local geometry at an adsorption site and on electronic structure. [35]

4.8.2. Auger electron spectroscopy (AES)

The Auger effect occurs, in competition with X-ray fluorescence, as a result of the intra-atomic reorganisation of electron states which follows ionisation of an atom. Auger peaks occur in XPS spectra but the major application of the effect employs ionisation by an electron beam (AES). The technique is similar to XPES in surface and elemental sensitivities and quantitative accuracy and has advantages of faster data acquisition and much smaller area of sampling. Chemical shifts are of magnitude similar to and in some case greater than the magnitudes of the shifts encountered in XPES. In practice, however, AES is not used for quantitative study of changes in chemical environment because of difficulties in measuring shifts with sufficient precision. An alternative approach recognises that for transitions involving the valence band or valence molecular orbitals, the chemical state of the atom will have a significant effect on the *shape* of the Auger line. Lineshape cannot yet be interpreted on a routine basis but at a qualitative level it can sometimes be used as a 'fingerprint' of a particular species.

While XPES has been applied extensively for the examination of changes in chemical environment, uses of AES have been concentrated on elemental identification and quantification, particularly in the case of chemisorption systems. The main areas of investigation have been promoters, catalyst deactivation and poisoning, segregation in alloys and the effects of adsorbates on surface composition.

4.9. Determination of spatial distribution of elements

4.9.1. Analytical electron microscopy

The incident beam in an electron microscope generates a number of signals which carry chemical information. The term analytical electron microscopy strictly refers to the detection of X-rays caused by sample ionisation in a dedicated STEM-type instrument or in an adequately equipped SEM (4.2.1.2D) or CTEM (see 4.9.2)

4.9.2. Energy dispersive X-ray spectroscopy (EDS, EDX)

Analysis of characteristic X-rays provides identification and quantification of elements with Z >10; improvements in X-ray detectors should reduce this limit to Z=6. The original electron probe microanalysis (EPMA) was essentially a low resolution SEM with an X-ray detector but the SEM mode suffers from two disadvantages: X-ray spatial resolution is relatively poor (1-2 μm) and quantitative analysis involves corrections for various processes within the thick specimen. With specimens sufficiently thin for TEM or STEM use (<200 nm) the X-ray resolution is improved (<50 nm) and a semi-quantitative analysis can be obtained without application of corrections; more rigorous treatment of the data gives relative concentrations to within about 5%, with a minimum detectable mass fraction of 0.3 wt%. [36]

4.9.3. Electron energy loss spectroscopy (EELS)

Ionisation of atomic core levels generates 'edges' in the scattered-electron energy distribution which identify the species involved. The technique is sensitive to elements with Z <10 and so complements X-ray microanalysis. Of the two methods, EELS has superior sensitivity and spatial resolution. It has been less widely used, however, because quantitative analysis requires very thin specimens and simple semi-quantitative measurements are not possible due to the complex nature of the spectrum background. Structure in the energy distribution above an edge contains EXAFS-type information (see EXELFS, section 4.4.3.4).

4.9.4. Scanning Auger microscopy (SAM)

If the incident beam in an Auger spectrometer is rastered over the specimen surface, the strength of a particular Auger transition can be used to generate an elemental map of the surface. SAM has the high surface sensitivity characteristic of AES and similar elemental sensitivity and spatial resolution (down to about 100 nm). [37]

4.10. Secondary ion mass spectroscopy (SIMS)

In SIMS a primary ion beam (1-20 keV) causes ejection (sputtering) of neutrals and ions from a solid specimen; the secondary ions are mass-analysed. In "static" mode, sampling is restricted to the first 1-3 atom layers at the surface by keeping the sputtering rate low (0.1 nm/hour). The ejected ions and ion-clusters give information on the nature and may give clues to the chemical state of species present.

In "dynamic" mode, the sputtering rate is high (1 μm/hour) and the technique gives a depth profile of the sample with a depth resolution of 2-10 nm and a lateral resolution of 1-60 μm. The advantages of SIMS are its ability to detect hydrogen and isotopically labelled species, its very low detection limit (10^{-5} atomic %) and its very large dynamic range (10^5-10^6). Its disadvantage is that sensitivity varies from element to element by up to 5 orders of magnitude and also depends very strongly on the chemical environment of a given species (matrix effect). Therefore, quantitative analysis is possible only in those relatively few cases where suitable calibrations are available.

4.11. Ion beam techniques (see also section 4.5)

Prompt nuclear reaction analysis (PNRA or NRA), light ions with energies below 2 MeV impinging on light target nuclei excite nuclear transmutations. As with RBS, both the identity and depth profile of the target species can be determined from an energy analysis of the emission. NRA complements RBS in being suitable for observation of elements with Z <20.

4.12. Depth profiling

The distribution of species normal to the surface can be obtained non-destructively by variation of the emission angle in XPS or AES (limited to a total depth of about 50 nm), by Rutherford backscattering spectrometry (applying only to elements with Z >10) and by nuclear reaction analysis (Z <20 only). Depth resolution in both RBS and NRA is in the range 5-50 nm.

Destructive methods involve mechanical and chemical erosion (low resolution) and ion sputtering, which is by far the most widely used of any of the depth profiling techniques. Surface atoms are progressively removed by ion bombardment and are analysed by SIMS. Alternatively, the residual surface may be analysed, generally by AES. The method is universally applicable and in principle is capable of near-atomic depth resolution. In practice, conversion of the observed signal, as a function of time, into concentration as a function of depth may not be easy for a complex system. It should be noted that the information obtained is reliable for the first layer, but for deeper layers the possibility of scrambling of the atomic layers under the influence of the ion beam must be taken into account.

5. CATALYTIC PROPERTIES

The correct evaluation of catalytic properties demands that heat and mass transfer limitations are eliminated or properly accounted for. It also demands that the catalyst is in the working state, as opposed to the transient state observed at the beginning of most catalytic tests. The absence of gas phase reactions or reactions catalysed by the reactor wall should also be verified. This must be kept in mind in the following, in which measurement methods, kinetic analyses including the influence of heat and mass transfer and deactivation or, more generally, time-dependent effects will be examined. Regeneration of catalysts will be examined at the end.

5.1. Reactor types and measurement methods [38]

The usefulness of a catalyst is expressed in terms of its activity, selectivity and life. The objective of catalyst testing in the laboratory is to provide information on one or more of these properties.

Laboratory reactors may be divided into steady state (continuous) and non-steady state. Steady state reactors may be further sub-divided into:

(1) plug flow,

(2) continuous stirred tank reactor, (also called gradientless flow reactor, or ideal back-mixed reactor, or perfect agitation reactor),

(3) fluidised bed.

Non-steady state reactors may be sub-divided into:

(4) batch,

(5) discontinuous flow, i.e., pulse or transient.

Other types of reactors, such as trickle bed or bubble (slurry) reactors, are used only in special cases for reactions of liquids with gases catalysed by solids.

An important criterium for the choice of reactors is whether they can operate in isothermal conditions. Data obtained in a non isothermal mode of operation are difficult to interpret.

Operation of the various reactors may be in integral or differential mode, and the latter may involve either a single pass or a recycle system using internal or external recycle.

These reactors give different types of information and the choice depends on the information required. The main uses of laboratory reactors are as follows: (The numbers refer to the types of reactor listed above and indicate the preferred choice.)

(a) to provide "activity values" in order to compare catalysts (1,2,3,4, to a limited extend 5);

(b) to study slow changes in activity (1,2);

(c) to study rapid changes in activity (5);

(d) to reveal the role of heat and mass-transfer (1,2,4);

(e) to derive the kinetic equation, i.e., to determine the influence of composition, pressure, temperature and contact time (1,2,4);

(f) to provide kinetic data for modelling of industrial reactors (1,2,4).

In the following sections the various types of reactors are described in more detail, as also are the methods used to introduce the reactants. This is followed by a brief summary containing suggestions on how to perform typical experimental measurements of catalytic properties.

5.1.1. Plug flow reactor

The plug flow reactor is usually made of a glass (Pyrex or quartz) or metal tube with a sintered disc or other appropriate means for supporting the solid catalyst, either alone or mixed with an inert diluent solid. One or several thermowells are located in the reactor to monitor the catalyst bed temperature. It is convenient to use thermocouples sliding inside thermowells to monitor axial or longitudinal temperature gradients. The reactor is heated in any convenient way, but should, as far as possible, behave isothermally. The reactants and any diluent gas are brought to a temperature close to that of the catalyst before passing through the catalyst bed. At the outlet of the reactor the reaction products are sampled, either as gases, liquids, or combinations of the two and analysed, usually by gas chromatography and/or by mass spectrometry.

This reactor operates under steady state conditions, but it can also provide information about the evolution of the catalytic activity with time during the approach to steady state. Ideally, in this reactor there is no mixing of fluid along the flow path and the contact time in the reactor is the same for all the elements of fluid.

One disadvantage of this, and indeed all continuous flow reactors, is that if the catalyst is very sensitive to poisons there is a risk that a small amount of poison in the reactant would accumulate on the catalyst during the experiment and cause major changes in activity and/or selectivity. In the laboratory this problem can usually be avoided by using very pure reactants.

The plug flow reactor may be operated in the differential or the integral mode. In the differential mode (small conversion) the whole catalyst can be considered to be exposed to the same concentration of reactants. The influence of products is generally weak, except when the catalyst is extremely sensitive to one particular product. The plug flow reactor operating in the differential mode is the simplest and most reliable way of determining the order of reaction with respect to reactants and products. This may be achieved by a systematic variation in the initial concentration of the reactants.

In the differential mode further major advantages are:

(i) it provides good kinetic data because of the short hold-up;

(ii) the low conversion helps minimise heat and mass transfer problems;

(iii) the influence of parameters such as temperature, pressure and concentration can be studied separately;

The major disadvantages of using a plug flow reactor in the differential mode are:

(i) at the small conversions required large errors in analysis can occur;

(ii) the technique is time consuming in kinetic measurements;

(iii) high gas velocities may be required to keep conversions low.

The integral plug flow reactor has the advantage that large conversions facilitate analysis and provide more accurate kinetic data. Disadvantages of the integral mode are problems in maintaining isothermal operation, the existence of concentration gradients, and possible heat and mass transfer limitations. Furthermore, accurate kinetic analysis of integral data is generally more difficult than for differential ones. In general in a laboratory reactor, in contrast to an industrial reactor, the depth of the catalyst bed is small, so that the reactor has a behaviour intermediate between that of a plug flow and a back-mixed flow reactor.

5.1.2. Continuous stirred tank reactor (CSTR)

The ideal continuous stirred tank reactor (back-mixed reactor) is free from intrareactor concentration gradients.

Truly differential reactors of this type provide the most useful kinetic data. However, as indicated above they suffer from problems of analysis, etc. The addition of a recycle stage permits one to overcome these problems since the conversion per pass remains differential but the overall conversion becomes large enough to be measured and reflects accurately the influence of products as well as that of the reactants. A drawback, however, concerns the design of experiments. At the beginning of the investigation, trial and error is necessary for obtaining the desired concentrations at the exit. In external recycle reactors the recycle stream is circulated by an external pump. In internal recycle reactors an impeller recycles the reaction mixture through a fixed bed of catalyst. Perfect mixing is achieved under most reaction conditions. The most widely known form of internal

recycle reactor is the Berty reactor. For gas phase reactions, a CSTR uses a spinning wire-mesh basket to hold the catalyst. Such a reactor is kinetically equivalent to a differential recycle reactor with a high recycle rate. The Carberry-type reactor is the best known example of a CSTR of this type.

The major uncertainty with this type of reactor is in determining the catalyst temperature. Usually this must be inferred from a knowlege of the heat of reaction, the rate of heat and mass transfer and the reaction rate. In view of this uncertainty regarding the catalyst temperature, these reactors are not recommended for the study of highly endothermic or exothermic reactions.

CSTR may also be used for liquid phase reactions. However, there can be severe problems with heat and mass transfer in such systems, and sampling of products can cause difficulties. For multiphase reactions it is necessary to ensure good contact between the gas and the liquid as well as between the liquid and the catalyst.

5.1.3. Fluidized bed reactor

When gases are blown from the bottom upwards through the catalyst bed a lifting force is created due to a pressure drop. This force increases with increasing linear flow rate. When the flow rate reaches a critical value, the catalyst becomes suspended in a state characterised by intensive chaotic motion of particles. The catalyst bed expands and acquires fluidity.

The major advantages of a fluidised bed are efficient heat transfer, ease of temperature control, and diminution of concentration gradient. Among the disadvantages are inhomogeneity of the bed (formation of gas bubbles), and a considerable back mixing. As a result, the selectivity of the catalytic process may decrease. To overcome, at least partly, these problems, special packing materials are introduced into the reactor. Another serious limitation is that the catalyst must possess high attrition resistance.

Fluidised bed reactors are rarely suitable for catalytic studies because of their relatively large volume, the large quantity of catalyst to use and the difficulty to control bubble agglomeration and instabilities. However, it is still almost irreplaceable for the testing of fluid bed cracking catalysts. On a laboratory scale a modification is applied in which an intensive mixing of particles is achieved by means of mechanical vibration. In this case, the gas flow rate can vary over a wide range, remaining below the critical value. This reactor combines advantages of a fluidised bed reactor and a gradientless reactor. In addition, it may have a small volume (up to 1 cm^3) and measurements can be made using a small quantity of the sample. Vibro-fluidised bed reactors are most effective for investigations of reaction mechanisms by the pulse method.

5.1.4. Batch reactor

The reactor is composed of a tank with heating, or cooling, and stirring devices. Catalyst is usually introduced into the reactor which is then closed, and liquid and gaseous reactants are introduced through valves. The partial pressures or concentrations of the reactants and products varies continuously throughout the experiment. The progress of the reaction may be followed by monitoring partial pressure changes or by analysis of samples by a special device.

This reactor is used with solid or liquid catalysts and with liquid reactants, or for gas/liquid reactions in the presence of solid catalysts. Batch reactors are also frequently used, as closed systems with circulation of the gas, for reactions of gases catalysed by solids. Nowadays, relatively few detailed kinetic studies are performed using

batch reactors. A common use of these reactors is for the rapid screening of catalysts particularily in high pressure/high temperature reactions.

The main advantages of a batch reactor are as follows. It is simple and allows rapid measurements. Many experiments can be performed in a short period of time. It is convenient when using pure, expensive, corrosive, or high boiling temperature chemicals. Its use is recommended if the catalyst is sensitive to traces of poisons since there is no accumulation effect. In principle, by varying the stirring conditions it is possible to investigate the influence of heat and mass transfer processes.

The main disadvantages of batch reactors, when used for high pressure experiments, are as follows. The large thermal capacity of the reactor limits the heating up and cooling down rates. As a consequence it is difficult to determine the time at which reaction commences. Sampling of products during an experimental run can be done but it is then necessary in some cases to ensure separation of the reactants from the catalyst. Finally, with liquid reactants it is rarely possible to control temperature and pressure independently. Thus, a batch reactor is not convenient for detailed kinetic studies since different parameters vary together (pressures or concentrations of reactants and products, evolution of the catalyst). Much care is needed in the introduction of reactants to obtain a good control over the starting time of the reaction. In practice this makes the study of fast reactions difficult.

5.1.5. Discontinuous flow reactor

The discontinuity of flow can be achieved by different methods such as injection of pulses of reactant(s) or changing abruptly the concentration of one or more reactants. The pulse reactor is often made of a tube through which a carrier gas flows at constant rate. At a specified time a slug of reactant is injected into the gas flow and the products emerging at the outlet of the reactor are analysed on-line.

The major advantages of this type of reactor are its simplicity and speed of operation, and the fact that only very small amounts of reactant and catalyst are required. This reactor gives an instantaneous image of the activity of a catalyst so it is useful for following any fast modification of the catalyst by the reaction itself or by a poison. It is particularly useful for studying the 'initial' activity of a catalyst. In addition, correlations with physical or spectroscopic observations are easier since in the pulse reactor the catalyst does not change too much during the course of the measurement. This type of reactor is convenient for rapid screening of catalysts and for studying catalysts which are sensitive to poisons or which change rapidly.

Disadvantages of the pulse reactor are as follows. It is not convenient for precise kinetic measurements. The pressures of reactant vary during the whole reaction and the kinetic treatment requires complex mathematical analysis. Steady state is not established during the period when the pulse is passing over the catalyst so selectivity data may be misleading. Material balance is difficult to establish.

Other types of discontinuous flow reactors may be used for transient kinetic studies in which, for example, isotopically labelled reactants are widely used in kinetic studies. This kind of investigation has been particularly developed in the case of discontinuous flow reactors. A different instrument called TAP (for Temporal Analysis of Products) permits extremely sensitive detection of intermediates or products. The results obtained with these various instruments can provide information about reaction mechanisms.

5.1.6. Reactants - Introduction methods

The batch reactor is generally heated once the reactants mixture has been added. A flash introduction of the reactant, previously brought to the reaction temperature can be envisaged. However, in order to control the starting time of the reaction, flash introduction of catalyst may alternatively be used.

With continuous flow reactors gases are usually introduced from compressed cylinders. A pump can be used to introduce liquids which are then vaporized and mixed with a carrier or reactant gas and passed through the catalyst. Viscous liquids may be preheated before pumping. Alternatively a double-pass saturator can be used in which the carrier or reactant gases are bubbled through a thermostatted liquid. This method offers the advantages that there are no mechanical parts and the reactant is already in the gas phase so preheating is easier. Ideally, the reactant pressure is dependent only on the temperature of the saturator and is not affected by the total pressure or the flow rate of the carrier gas. A saturator may be used with reactors working even at high pressures.

5.1.7. Typical experimental parameters used in catalyst testing

5.1.7.1. *Reactor*

A typical laboratory flow reactor would have a volume of up to about a few cm^3 and a cross-sectional area preferably less than a cm^2. The mass of catalyst used depends on its activity but would typically be between 0.05 and 3.0 g. The choice of particle size is important. For laboratory reactors small particles (0.1 mm) are recommended for minimizing problems. Generally accepted rules are the following:

(i) the ratio of the height of the catalytic bed to the reactor diameters should be around 10:1.

(ii) the ratio of the reactor diameter to granule or particle size be around 10:1. These conditions are more likely to ensure good flow conditions and to avoid channeling.

If the catalytic reaction is strongly exothermic it may be useful to dilute the catalyst with an inert material having a similar particle size to the catalyst. Preheating of the feedstock is rarely necessary in laboratory reactors. When required, a bed of inert material (e.g., carborundum) can be used. The reactor should generally be mounted vertically. It is advisable to measure the temperature of the catalyst bed directly, particularly for reactions which are strongly exothermic or endothermic. This may be done by mounting a thermocouple in the centre of the catalyst bed, or by inserting a thermocouple into a thermowell in the side of the reactor tube. It is prudent to check the temperature profile along a catalyst bed. It is also advisable to check that the thermocouple itself has no catalytic activity if it is inserted directly in the bed.

5.1.7.2. *Reactants*

In laboratory reactors the flow of reactants is determined to a large extent by the size of apparatus and amount of catalyst used. A space time of about 0.1 - 1 s is common. In general, normal laboratory reagents will not contain any impurities likely to seriously affect the measurements. However, it is always advisable to check the level and the nature of the impurities. In some circumstances relatively impure feedstocks may be perfectly satisfactory. Sometimes the reactants are diluted by addition of an inert material. (It is prudent to confirm that the chosen diluent is inert.) There are two instances where a diluent may be used:

(a) to reduce temperature changes caused by the thermal effects of a reaction; but this has only a limited effect;

(b) to investigate the influence of partial pressures in kinetic experiments.

In most laboratory kinetic studies ambient pressure is used. If the pressure of one reactant is varied over a wide range, in order to maintain the pressure of a second reactant constant it is necessary to add an inert diluent to bring the total pressure up to ambient pressure. The choice of pressure should take account ot the type of reaction under investigation.

5.1.7.3. *Catalyst*

No general rules can be given concerning the correct method of handling the catalyst before use. It should be recognised, however, that the conditions used in drying, storing, reducing, etc. a catalyst may affect its properties. Whether a fresh charge of catalyst should be used for each separate catalyst test (for example, a fresh sample used at each test temperature) depends on the stability of the catalyst. If the catalytic properties appear to be invariant with time there should be no need to change the sample. Replicating an activity measurement at the beginning and at the end of the series of experiments indicates whether the catalyst is stable. However, it is advisable to make changes in temperature in a random fashion, which is more likely to reveal time-dependent effects. If the catalytic properties change rapidly with time it may be necessary to use a fresh sample in each experiment.

5.1.7.4. *Problems of heat and mass-transfer*

Very careful attention must be given to the possibility of heat and mass-transfer problems and all due precautions should be taken (see next section). For some reactions, such as oxidation, where heat transfer may be important, one must find, and use, experimental conditions which avoid these effects.

Experimentally, the observation of a small activation energy, or a sharp decrease in the activation energy at higher temperatures, may indicate a serious diffusion problem. However, this should only be taken as a cautionary sign since other causes may exist. In particular, the influence of heat and mass transfer on the reaction kinetics should be checked experimentally by adequate procedures, if available, or theoretically using the appropriate mathematical relationships.

5.2. Kinetic analysis [39-47]

5.2.1. Determination of the reaction rate

From the amount of the reactant converted or the product formed (degree of conversion), or more frequently from the dependence of these quantities on the time variable, the rate of production (consumption), R_j, of a chosen reaction component and from it the reaction rate, r, may be evaluated, based on the mass balance for the given reactor type.

For the reactor types most commonly used in kinetic studies we obtain the following mass balance equations for reaction component j chosen as the key component:

(1) *for ideal plug flow reactor*:

$$R_j = -\mathrm{d}X/\mathrm{d}(Q/F_{j,0}) \qquad (1)$$

where X is the fractional conversion, Q is the amount of the catalyst and $F_{j,0}$ is the molar flow rate of the component j at the inlet of the reactor; the term $Q/F_{j,0}$ is often referred to as the reciprocal space velocity or space time [1].

(2) *for a CSTR reactor*:

$$R_j = -(F_{j,0} - F_j)/Q \qquad (2)$$

with the same meaning for the symbols as in Eq. (1); F_j is the molar flow rate of the balanced component j at the outlet of the reactor;

(3) *for a perfectly stirred batch reactor*:

$$R_j = (\mathrm{d}n_j/\mathrm{d}t)/Q \qquad (3)$$

where n_j is the amount of reactant j, and t is reaction time.

Eqs. (1) to (3) relate the rate of production R_j of the balanced reaction component j to the molar amounts or their derivatives with respect to the time variable (reaction time or space time, see above). From the algebraic Eq. (2) for the CSTR reactor the rate of production, R_j, may be calculated very simply by introducing the molar flow rates at the inlet and outlet of the reactor; these quantities are easily derived from the known flow rate and the analytically determined composition of the reaction mixture. With a plug-flow or with a batch reactor we either have to limit the changes of conversion X or mole amount n_j to very low values so that the derivatives $\mathrm{d}X_j/\mathrm{d}(Q/F_{j,0})$ or $\mathrm{d}n_j/\mathrm{d}t$ could be approximated by differences $\Delta X_j/\Delta(Q/F_{j,0})$ or $\Delta n_j/\Delta t$, (differential mode of operation), or to measure experimentally the dependence of X_j or n_j on the space or reaction time in a broader region; this dependence is then differentiated graphically or numerically.

The individual values of the rates of production R_j of the reaction components in a given reaction, obtained in the way just described, depend, however, on the reaction stoichiometry. In a single (stoichiometrically simple) reaction

$$\sum_{j=1}^{s} \upsilon_j A_j = 0 \qquad (4)$$

where s is the number of reaction components each identified by a subscript j; A_j is the amount of component j; υ_j is the stoichiometric coefficient of the component j, negative for reactants, positive for products. The rates of production of reaction components are related in a very simple way:

$$\upsilon_1^{-1}R_1 = \upsilon_2^{-1}R_2 = \text{-----} \upsilon_j^{-1}R_j = \upsilon_s^{-1}R_s = r \qquad (5)$$

from which it follows that the rate of production R_j divided by the stoichiometric coefficient υ_j has the same value for all the s chemical species involved in the reaction. Since the value $\upsilon_j^{-1}R_j$ is independent of the reaction stoichiometry and of the choice of the balanced (key) component, it is called rate of reaction or simply reaction rate r.

In a reaction network in which several stoichiometrically simple reactions take place, Eqs. (1) to (3) are still used for the primary treatment of the reactor data but the overall rate of production obtained for the j-th component is here equal to the algebraic sum of the rates of production in all the reactions in which the j-th component is formed or consumed. In such a case the evaluation of the reaction rates r of the individual reactions of the network from the rates of production R_j of the key components is more complicated.

As seen from Eqs. (1) to (3), the rate of production and, consequently, the rate of catalytic reaction are related to the quantity of catalyst Q which may, for example, be expressed as the mass (m_c), volume (V_c) or the surface area (A_c) of the solid catalyst. The numerical values of the corresponding specific reaction rates (r_m, r_v, r_A) naturally differ from each other depending on the quantity to which they are related.

5.2.2. Rate equations

The rate of a reaction is generally a function of the temperature and concentrations of reactants, products and other substances if present. The kinetic equation thus obtained is commonly called the rate equation or the rate law. To find the form of the kinetic equation and the values of its constants is the main task of the kinetic analysis. The first stage of the procedure consists in an experimental measurement of the reaction rate or the conversion in an adequate region of experimental variables. It is advisable to keep the temperature constant and to vary the concentrations; this may be repeated for other temperatures if the temperature dependence of the kinetic constants is to be evaluated. The influence of the concentration of each reaction component can be measured separately and the reaction order with respect to it determined by varying one concentration and keeping the others constant. Note, however, that introducing this or any other binding condition, such as constant ratio or constant total concentration of reaction components, will reduce the actual number of independent variables. To avoid the loss of information caused by this approach, it is possible to vary the concentrations of reaction components quite randomly in such a manner that the space defined by the extreme values of the investigated concentrations might be covered.

The data are fitted to several equations and the best fit selected. The equations are proposed either on an empirical basis or they may be derived on the basis of some reaction mechanism [39-47].

Mathematically, both empirical and model rate equations for heterogeneous catalytic reactions have either the form of a power law (power-law type rate equations):

$$r = k\, c_A^{\,m}\, c_B^{\,n} \ldots\ldots \tag{6}$$

or they are a fractional function with a polynomial in the denominator:

$$r = \frac{k\, C_A^{\,a}\, C_B^{\,b}}{[1 + (K_A C_A)^{\alpha} + (K_B C_B)^{\beta} \ldots\ldots]^{d}} \tag{7}$$

One also uses combinations of the two forms (e.g., multiplying forms of eq. (6) and eq. (7).

Model rate equations are rate equations based on commonly accepted rate expressions used in the field of catalysis. Very frequently, but not always correctly, the equations of this type (7) are called Langmuir-

Hinshelwood type rate equations. In Eqs. (6) and (7) the indices A and B denote the reactants but very often the concentrations of reaction products also appear in the equations (in equations of type (7), usually in the denominator).

The proportionality factor k is called the experimental rate constant; with catalytic reactions, this constant is frequently a complex quantity which may be a product of rate constants of several steps or may include equilibrium constants of the fast steps. The exponents m, n, ... in the power-law equations may be any fraction or small integer (positive, negative or zero). The constants K_A, K_B, - in the denominator of the equations of type (7) are often but not always related to adsorption equilibrium constants. While they have to be evaluated from the experimental data, the values of exponents a, b, α, β, - and d are derived from the assumed mechanism in the case of model rate equations. In empirical rate equations these constants can attain any value (fractional or small integer, usually positive) and are either postulated or determined by the data treatment.

The rate equation for a system in which the back reaction is not negligible is given by the difference between rate equations for the two directions.

5.2.3. Selection of a suitable form of the rate equation and evaluation of constants

These two tasks are related because the selection, based on the fit of the equation to experimental data, is only possible after the evaluation of the constants.

On the basis of experience, analogy, or information obtained from fundamental chemical mechanisms, one constructs *a priori* several possible, or likely, model kinetic equations. These models are then compared, according to the methodology described above, to the experimental data.

The criterion of the fit is most frequently the sum of squared deviations (or of their relative values) between the calculated (y_i') and measured (y_i) values of the dependent variable throughout all the experiments performed (N):

$$Q(\kappa) = \sum_{i=1}^{i=N} (y_i' - y_i)^2 \quad \text{or} \quad Q(\kappa) = \sum_{i=1}^{i=N} (y_i' - y_i)^2/y_i^2 \tag{8}$$

The problem consists in seeking such a combination of the values of constants κ which gives the minimum value of Q (Q_{min}). Before computers became commonly available, the kinetic equations had usually been transformed into a linear form and the linear regression ("least squares method") had been applied to find the best set of constants. This procedure is not statistically correct in most cases. Therefore, only the non-linear regression method can be recommended to optimize constants in kinetic equations that have a non-linear form [48-51].

The dependent variable y is most frequently the reaction rate; independent variables are the concentration or pressure of reaction components, temperature and time. If in some cases the so-called integral data (reactant concentrations or conversion versus time variable) are to be treated, a differential kinetic equation obtained by the combination of a rate equation with the mass balance equation (1) or (3) for the given type of reactor is used. The differential equation is integrated numerically, and the values obtained are compared with experimental data.

If several kinetic equations are compared the one which fits best will be that which exhibits the lowest value of Q_{min}. However, the difference in the Q_{min} values for some equations may be statistically insignificant and then further experimentation with increased accuracy is necessary and another region of experimental variables has to be chosen where the discrimination between rival kinetic equations may be easier, provided no change of mechanism takes place.

For better model discrimination and/or parameter estimation, sequential methods for computer designed plans of experiments have been proposed [52]. They take advantage of the information obtained from the previous experiments and plan the new experiments in the region of independent variables where the maximum difference of the dependent variable can be expected.

Even with advanced methods, several models may satisfy the Q_{min} requirement. Further discrimination necessitates additional information. This may come from experience, analogy, measurements using special techniques, such as isotope labelling, and fundamental knowledge on chemical mechanisms.

If the kinetic experiments are performed at different temperatures, the temperature dependence of the constants obtained can be determined. With empirical rate equations, one can obtain any dependence of the constants on temperature. With model rate equations the constants should have a certain physical meaning and behave, in dependence on the temperature, according to the theory. Thus, the rate constants should follow the Arrhenius equation:

$$k = A \exp(-E/RT) \tag{9}$$

where A is the pre-exponential factor, and E is the activation energy. (With catalytic reactions E is very frequently a complex quantity and is more aptly called "apparent activation energy"). The equilibrium constants of fast steps, if present in the rate equation, should obey the van't Hoff equation

$$K = B \exp(-\Delta H/RT) \tag{10}$$

where ΔH is the reaction enthalpy of the fast step in the reaction mechanism. For evaluating the parameters of Eqs. (9) and (10), the non-linear regression method is again recommended.

Sometimes, the reaction rate at constant concentrations instead of the rate constant is correlated with temperature by means of the Arrhenius equation. However, this is not justified with most catalytic reactions since each constant in the rate equation may be temperature dependent and, consequently, the reaction rate is a very complicated function of temperature. Therefore, attempts to correlate information obtained from log r versus $1/T$ plots might be misleading.

5.2.4. Heat and mass transfer effects

Heterogeneous catalytic reactions occurring on the solid-fluid interface may be affected by the heat and mass transfer to and from the interface. We distinguish external transfer effects (from the bulk of the reactant fluid to the outer surface of the catalyst particle) and internal transfer effects (from the outer to the inner surface of the porous catalyst particle). These physical processes take place simultaneously with the catalytic reaction on the

surface. If they are fast enough, the rate measured is the intrinsic rate of the chemical transformation (kinetic region); if not, the measured kinetics is influenced by mass and heat transfer effects. Therefore, before starting kinetic measurements we have to check whether the experimental equipment and reaction conditions used allow work in the kinetic region and if not to change the conditions in order to suppress the transfer effects. A priori criteria can be obtained along the lines indicated in sections 5.2.4.1. and 5.2.4.2. below. Some semiempirical criteria based on experiments may also be adopted, such as the interpretation of data obtained by changing the particle size, the flow rate, agitation, etc.; details of these may be found in specialized literature [53,54]. Special geometrical arrangements are used to detect and/or measure mass transfer limitation: single pellet or "single-string-pellet" reactors.

The mass transfer effects cause, in general, a decrease of the measured reaction rate. The heat transfer effects may lead in the case of endothermic reactions also to a decrease of the equilibrium value and the resulting negative effect may be more pronounced. With exothermic reactions, an insufficient heat removal causes an increase of the reaction rate. In such a case, if both the heat and mass transfer effects are operating, they can either compensate each other or one of them prevails. In the case of internal transfer, mass transport effects are usually more important than heat transport, but in the case of external transfer the opposite prevails. Heat transport effects frequently play a more important role, especially in catalytic reactions of gases. The influence of heat and mass transfer effects should be evaluated before the determination of kinetics. These effects should preferably be completely eliminated.

5.2.4.1. *Internal mass and heat transfer*

The effect of mass and heat transport to and from the inner particle surface on the reaction rate can be characterized by the effectiveness factor, η, i.e., by the ratio of the effective reaction rate measured on the catalyst particle under study (r_{ef}) to the rate of the reaction in the kinetic region (r_{kin})

$$\eta = r_{ef}/r_{kin} \tag{11}$$

Knowledge of the reaction rate free of any diffusional effect, r_{kin}, is thus necessary in evaluating experimentally the magnitude of these effects. The effectiveness factor for an isothermal situation can also be calculated approximately by means of the Thiele modulus [39], but knowledge of the kinetics in the diffusion-free region and of the effective diffusion coefficient characterizing the transport properties of the porous material is necessary. The effect of internal diffusion increases with increasing catalyst activity, reaction temperature and catalyst particle size, and with decreasing pore size of the catalyst.

5.2.4.2. *External mass and heat transfer*

The difference between the concentrations of a reactant (or temperatures) at the outer particle surface and in the bulk of the reaction mixture may become important if the rate of diffusion of this reactant (or heat transfer) through the laminar film surrounding the particles is lower than the rate of the reactant (or heat) consumption (production) by the chemical reaction. The thickness of the laminar film and the concentration (temperature) differences are smaller the more turbulent is the reactant fluid. Therefore, the magnitude of the effect of external

mass and heat transfer also depends on the type and the geometry of the reactor used and kinetic data obtained in the region of external transfer in one reactor cannot be applied to another reactor. Thus, data free of external transfer effects should be used for a reliable kinetic analysis. Such data are obtained preferably in flow reactors with high flow rates and low reactant conversion per pass, e.g., in the continuous stirred tank reactor or a tubular flow reactor working under differential conditions (see Section 5.1).

5.3. Inhibition of catalytic action

This section concerns the partial or total inhibition of catalytic action. Substances causing this inhibition ("inhibitory" or "deactivating" substances) can be conveniently indicated by IS. The alteration, reduction, or suppression of the catalytic activity can be a consequence of:

* adsorption of IS on active sites (as);
* modification of as (due to reaction with IS);
* restriction of physical access to as due to the presence of layers or particles of IS.

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

(a) the nature of the IS acting on the catalyst,

(b) an adequate relationship between the quantity of IS and the catalytic properties,

(c) time-dependent effects on activity, selectivity, etc., due to the presence, or a modification of concentration, of IS (decrease of catalytic activity with time, total or partial recovery of catalytic properties after removal of IS from the feed, etc.).

Because of the complexity of the phenomena taking place on a working catalyst information under (c) is usually incompletely analysed with respect to the role of IS, and reflects the combined effect of several categories of processes. For this reason, most of the corresponding discussion will be reserved for sections 5.4 and 5.5.

5.3.1. Identification of the inhibiting substances

Full characterisation of catalysts with respect to the influence of IS requires that all the IS be identified chemically and their mode of action understood. Because of the variety of cases observed, no universal method exists for identifying IS. It must be clear that the role of any IS is specific to the catalyst and reaction studied.

5.3.2. Identification of the mode of action of the IS

IS, and especially poisons and inhibitors, can have strong effects at very low surface coverages (a few percent or less of surface area). Except for inhibitors, they have a cumulative effect.

Chemical identification of IS can be achieved by consideration of the following points. IS may be any substance that normally or accidentally enters into contact with catalysts, e.g., impurities in the feed, impurities released from the equipment, leaks. IS may also be formed by transformation of the reactants in contact with the catalyst (e.g., coke formation).

Extremely sensitive analysis may be mandatory. As the IS usually (but not always, e.g., dust) accumulates on catalysts and, more specifically, on their surface, surface sensitive techniques are particularly useful.

In essence, three criteria permit identification of the category (poison, inhibitor, fouling agent) to which IS belongs (see Table 1).

TABLE 1

Quantities	Action	Interaction with catalyst	Nature of IS
small	irreversible	strong	POISON
small	reversible	weak	INHIBITOR
large	either	weak	FOULING AGENT

Chemical, and especially, surface analysis provides information concerning the first column in Table 1, namely, quantity. Activity/selectivity measurements provide information on the reversibility of the mode of action. The identification of the nature of the interaction with the catalyst depends on spectroscopic methods: differences in electron spectroscopies, IR, Raman, ESR spectroscopies, etc.

5.3.3. Characterisation of catalysts with respect to their response to IS

Characterisation of catalysts with respect to their propensity to be inhibited by IS must take into account the fact that the phenomena depend upon the whole catalytic reaction system (catalysts, degree of ageing and/or poisoning, inhibiting effects, operating conditions) and upon the whole succession of reactions to which the catalysts have been subjected.

Reported results on sensitivity to inhibition should clearly indicate to what stage of catalyst life the reported results correspond. The most important results with respect to fundamental studies (rational interpretation of the observed effects) and practical applications correspond to those obtained on catalysts having attained an activity-selectivity plateau.

There exist cases where selectivity is markedly improved by inhibition because of the suppression of side reactions.

5.3.4. Poisons

Sensitivity to poisons depends upon three factors:

* the number of active centres in the catalyst;
* the strength of adsorption of the poison on the active centres;
* the effectiveness of adsorbed poisons for inhibiting the catalytic activity.

The effectiveness of an adsorbed poison depends on the ratio x_0/x_t, where x_0 is the amount of poison per active centre necessary to inhibit catalytic action, and x_t is the number of active centres.

The minimum concentration required to eliminate the catalytic activity is one possible measure of the sensitivity of a catalyst to a poison. Sensitivity to poisonning is most properly defined by the amount, n_p, of the poison adsorbed on a unit amount of catalysts which causes a given fractional decrease of the catalytic activity ($\alpha = (a_0 - a_p)/a_0$), where a_0 and a_p are the activities in the absence or presence of poison, respectively): α/n_p is a measure of the sensitivity to poisonning. One may also use the ratio of a to the concentration c_p of the poison in the feed, namely α/c_p, but this is less precise, as this depends on the adsorption coefficient of the poison.

The basic values α/c_p, α/n_p and x_o/x_t have to be complemented, in most cases, by two types of characteristics of the catalyst. The first concerns the sensitivity of selectivity. Parameters similar to those mentioned in the previous paragraph must be determined for all selectivities of interest, i.e., all different reactions. The second concerns the possible variation of the magnitude of the effect, on activity and selectivity, of a poison as a function of surface coverage (or degree of inhibition). Ideally the whole curve α/c_p vs c_p, α/n_p vs n_p or α vs x/x_t should be constructed for all parallel and consecutive reactions taking place. An acceptable way of characterizing a catalyst is to report the initial sensitivity to deactivation (as indicated above), the points of zero activity, and a few characteristic intermediate points, e.g. c_p or n_p values, when a reaches certain values, such as 1/2, or some other fraction, or a values when c_p or n_p equals a given fraction of the value leading to zero activity.

When dealing with complex catalysts (multifunctional, supported, etc.) and with beds of catalyst, the characterization of the effect of poisons also involves the localization in space of the poisons (e.g., is the poison attached to the metal or the support?, is it uniformly distributed over all the catalyst pellet or selectively deposited?). The concentration of a true poison exhibits a decreasing profile over the catalyst bed.

Characterization thus involves analytical electron microscopy, ordinary microprobe analysis or other techniques for localizing elements or chemical compounds (Scanning Auger Spectroscopy, Raman Microprobe, Laser Microprobe Mass Spectrometry). It also requires, in most cases, some physical separation of the catalyst for separate analysis (e.g., near surface parts and centre of pellets, by peeling or progressive abrasion; pellets present at various heights in the catalyst bed, etc.).

5.3.5. Inhibitors

The action of inhibitors is intermediate between very strong irreversible poisoning and the normal competition between molecules for a given active site. The sensitivity to inhibitors can thus be expressed either as in the case of poisons (and then α/c_p can be used), or as in the case of competition (e.g., by a classical Langmuir-Hinshelwood formulation). In the latter case, for example, the value, or relative value, of the adsorption coefficient could characterize the inhibitor.

As the response of catalysts to inhibitors may not be instantaneous, especially if some chromatographic effect in the bed takes place, it is also necessary to characterize the catalyst with respect to the rate at which activity decays when the catalyst is contacted with a given concentration of inhibitor, or recovers, after the addition of the inhibitor is discontinued (see section 5.4).

5.3.6. Fouling agents

The inhibiting influence of fouling agents is not related in a simple way to the quantity of deposited substance. The reason is that the relationship between this quantity, w_p, and activity depends on the nature and texture of the catalyst, the nature and concentration of the feed constituents, the temperature and operating conditions, and the rate of build up of the fouling deposit (in practical terms: feed rate/catalyst weight ratio). It is thus necessary to indicate clearly the value of all these parameters when expressing the rate vs deposited quantity ratio. It is recommended that weights should be used (per unit weight of catalyst) to express the quantity of fouling agent as, usually, the composition of the deposit is not exactly known.

As the quantity of fouling agents necessary to bring about a noticeable change in activity/selectivity is relatively large, characterization by methods other than catalytic activity measurements is useful. The rate of build-up of the deposits of fouling agent can be measured gravimetrically. Microscopic or analytical electron microscope measurements can help locate the deposits (pores, etc.). In certain cases Raman Microprobe Analysis and Laser Microprobe Mass Spectrometry can also give valuable information.

In the case of carbon (coke), the variation of concentration over the catalyst bed gives an indication of the origin of the deposit. A decreasing profile implies that some compound in the feed is responsible. If the main reactant brings about coke formation, one has a so-called "parallel coking". An increasing profile indicates that coke is formed from a reaction product ("consecutive coking").

5.4. Deactivation of catalysts and time-dependent effects

The composition, structure, texture, surface state, activity and selectivity of catalysts change continuously, at rapid or slow rates according to conditions, during catalytic work. One type of change of paramount importance for characterisation of catalysts, especially for practical applications, is the deactivation behaviour. Two other aspects have also to be considered, namely (i) the usually rapid changes that catalytic activity and selectivity undergo in the first few minutes, hours or sometimes days of work (initial adjustment to catalytic operation), and (ii) the response to changing operating conditions (response to change).

The kinetics of the reaction are dictated by the concentration of reactants at the active site. If there are mass transfer limitations in the system, reactant concentration at the active site concentration is not the same as the bulk concentration, and the rate will vary. Mass transfer limitations may exist in a given catalyst or may be produced during operation - for example, by the deposition of coke or the closure of pores.

The net result of any or all of these factors is that the catalyst may lose activity and/or selectivity and the catalyst will have to be regenerated/replaced after a period of time.

Deactivation, or more generally, changes in activity/selectivity, reflect changes in composition, structure, texture and surface state. These changes are due to processes belonging to seven main categories, all of which may interact with each other:

(a) poisoning;
(b) inhibition;
(c) fouling;
(d) sintering;
(e) chemical reactions;
(f) restructuring of the surface;
(g) physical action.

Poisoning, inhibition and fouling have been dealt with already. Sintering corresponds to diminution of surface area of the active phase, modifiers, supports, etc.

Chemical reactions involve reaction with feed (e.g., reaction with a poison; reduction, in the case of oxidation catalysts), intermediary or final products (e.g. carbide formation), or reaction between catalyst components.

Restructuring refers to changes of the surface which do not involve any of the previous processes (or are too subtle to be detected): 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, etc.

Physical action, e.g., by attrition, may result in the loss of the active components of the catalyst.

There is often a coupling together of these processes: the rate of one process depends on the rate at which another process takes place. There are two general consequences of these coupling effects:

* time-dependent changes, and especially deactivation, need comprehensive characterisation;
* characterisation of the propensity of catalysts to deactivation through the use of accelerated test needs special care in order to avoid erroneous interpretations (see 5.4.3).

5.4.1. Deactivation: overall characterization

The overall effect of deactivation is characterised by the activity and selectivity variations as a function of time under well defined conditions. Under isothermal conditions the results may be presented as an activity/selectivity vs. time plot. In large pilot plants and in commercial units the operation is conducted in such a way that one parameter characterising the product is kept constant (yield of a given chemical, or given global property). Temperature T has to be raised to maintain the parameter constant. A T vs. t plot is obtained. Neither kind of measurement gives unequivocal information with respect to the characterisation of deactivation. Ideally both should be used. The second method of measurement has necessarily to be completed by the determination of the variation in selectivity with time. The shape of the activity vs. t or T vs. t curves is a very useful characteristic of a catalyst.

5.4.2. Physico-chemical characterization in deactivation studies

The methodology for characterising deactivated catalysts by physico-chemical techniques has to be developed for each specific case but should involve all the techniques generally used for characterising catalysts and studying inhibitory effects.

Sampling should be guided by three principles:

(a) samples should be protected from contamination;

(b) samples should be taken from various places in the reactor;

(c) characterization should involve the study of different pellets of catalyst since because of preparation/composition differences, the behaviour of catalyst can vary from pellet to pellet, at the same place in a reactor. Extreme care should be taken that one effect (among the many parallel and coupled changes) does not bring about errors in the measurement of another effect. A typical example concerns the use of XPES for measuring contamination by poisons or loss of dispersion: the masking effect of a fouling agent which is difficult to detect could lead to enormous errors.

5.4.3. Accelerated tests

In view of the usually very long time scale of deactivation phenomena, one has often to resort to accelerated tests. This is absolutely necessary when industrial development is contemplated. As deactivation is the result of several different processes, very often coupled together, the accelerated test cannot fully represent the non-accelerated phenomenon. For example, if higher temperatures are used for acceleration, the balance of the various

TABLE 2

Parameters modified	Test potentially valid if deactivation due to:
temperature:	sintering; solid state reaction; fouling
space velocity:	fouling; coking
inhibitory substances:	fouling; coking, poisoning
increased concentration of inhibiting substances:	fouling; coking; poisoning
modified feed composition:	fouling; coking; poisoning
artificial deposition of fouling substances:	fouling
vibration:	attrition

elementary processes will be altered, because of differences in activation energy. Some accelerated tests are generally better than others, see Table 2. The real significance of each type of test has to be assessed in each case.

5.5. Regeneration

Regeneration consists of: (i) removal of inhibiting substances IS: sometimes poisons, most often inhibitors or fouling agents, e.g., coke; (ii) redispersion of the active species, or (iii) both. Regeneration procedures are often specific to the catalyst and the species causing deactivation. With respect to regeneration, procedures are described precisely by catalyst manufacturers, for each type of important industrial catalyst. Procedures for laboratory catalysts must also be adapted to each specific case.

5.5.1. Preliminary treatment

In many cases, liquid, semi-liquid, or waxy substances adhere to the catalyst and fill the pores. They must be eliminated before removal of the real inhibiting substance.

5.5.2. Removal of inhibitory substances (IS)

Inhibition, or catalyst poisoning, results from reactions between IS and as (see 5.3). Often, the amount of IS adsorbed depends on the partial pressure of IS in the gas phase and on the strength of adsorption. As a result, the IS may sometimes be 'stripped' from the catalyst by passage of inert gas at a moderate temperature. If a chemical bond has formed between IS and as, chemical treatment may also remove IS. The most common example of this is the removal of sulfur from the surface by passage of hydrogen.

Some care must be exercised in selecting the chemical treatment. Thus, for example, metal sulfides can be converted to non-inhibitory (but usually inactive) metal sulfates by reaction with O_2. However, sulfates remain in the reactor and, in some cases, can be re-converted to sulfides on re-admission of H_2.

5.5.3. Removal of coke

Coke, deposited on a catalyst, may be removed by one of several reactions: oxidation, reaction with water to form carbon monoxide and hydrogen methanation, and the Boudouart reactions.

Of these, the oxidation reaction is most efficient, but produces heat. This may raise the temperature of the catalyst and result in sintering. Good temperature-programming and control during de-coking is essential. Very sensitive catalysts may be regenerated with H_2, but the rates of the reaction are slow and the process inefficient.

Regeneration with steam is more efficient and is endothermic. However, sintering of catalysts is accelerated by steam. As a result, regeneration procedures are a compromise. Often mixtures of air and steam are used.

5.5.4. Removal of foulants

Liquid or semi-liquid foulants may be accumulated on the catalyst. In this case, it is necessary to 'strip' the catalyst in an inert gas flow at moderate temperature before removing material as described for the removal of coke.

Solid inorganic foulants may also accumulate on the catalyst. Little can be done to remove such foulants except by mechanical means. This is usually inefficient, and replacement of catalyst is often necessary.

Recently, supercritical fluids (e.g. CO_2) have been proposed for removing coke and fouling agents.

5.5.5. Redispersion

In a few cases it is possible to redisperse sintered materials on a catalyst. The procedures involved are dependent on the nature of the system. In typical examples, dispersion is increased by the formation of oxides or oxychlorides. The operation involves careful control of regeneration conditions bearing in mind the nature of the catalyst, the IS, and the maximum allowable temperature under regeneration conditions.

5.5.6. General

There is considerable interest in extending catalyst life, accelerating regeneration and maintaining activity, factors which are often ignored in a laboratory scale investigation.

Regeneration is widely practised in industry, particularly in the context of coke removal. Various plant designs have been developed to overcome this problem, ranging from continuous deactivation/regeneration to moving beds of catalyst. A recent trend is to remove the used catalyst from the reactor, to ship it to special plants where it is regenerated (ex-situ regeneration). Catalyst regeneration can often be efficient provided good temperature control is maintained. It is not always economic to regenerate completely, and 90% of the original activity is often accepted. Post-regeneration treatment is often necessary before the catalyst is brought back to life.

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LIST OF ACRONYMS

AES : Auger electron spectroscopy

BET : Brunauer, Emmett, Teller (method)

BNS : nuclear backscattering spectroscopy

CSTR : continuous stirred tank reactor

CTEM : conventional transmission electron microscopy

DRIFT : Diffuse reflectance infrared Fourier transform

DRS : diffuse reflectance spectroscopy

EDS : energy dispersive X-ray spectroscopy

EDX : energy dispersive X-ray spectroscopy

EELS : electron energy loss spectroscopy

EELS : high resolution electron energy loss spectroscopy

EPMA : electron probe microanalysis

ESCA : electron spectroscopy for chemical analysis

ESR : electron spin resonance

EXAFS : extended X-ray absorption fine structure

EXELFS : extended energy loss fine structure

FT : Fourier transform

FTIR : Fourier transform Raman spectroscopy

HEIS : high-energy ion scattering

HREELS : high resolution electron energy loss spectroscopy

HREM : high resolution electron microscopy

INS : inelastic neutron scattering spectroscopy

IR : transmission infrared spectroscopy

IRAS : reflection-absorption infrared spectroscopy

ISS : ion scattering spectroscopy

LEIS : low-energy ion scattering

MASNMR : magic angle spinning nuclear magnetic resonance

NEXAFS : near-edge X-ray absorption fine structure (synonym : XANES)

NMR : nuclear magnetic resonance

NRA : prompt nuclear reaction analysis

PAS : photoacoustic spectroscopy

PNRA : prompt nuclear reaction analysis

RAIRS : reflection-absorption infrared spectroscopy

RBS : Rutherford backscattering spectroscopy

RED : radial electron distribution

REM : reflection electron microscopy

RHEED : reflection high energy electron diffraction

SAM : scanning Auger microscopy

SAXS : small angle X-ray scattering

SEELFS : surface-sensitive energy loss fine structure

SEM : scanning electron microscopy

SERS : surface enhanced Raman scattering

SEXAFS : surface extended X-ray absorption fine structure

SIMS : secondary ion mass spectroscopy

STEM : scanning transmission electron microscopy

TEM : transmission electron microscopy

UPES : ultra-violet photoelectron spectroscopy

UPS : ultra-violet photoelectron spectroscopy

WAXS : wide-angle X-ray scattering

XANES : X-ray absorption near-edge structure (synonym : NEXAFS)

XPES : X-ray photoelectron spectroscopy

XPS : X-ray photoelectron spectroscopy

XRD : X-ray diffraction