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Fundamentals in the preparation of heterogeneous catalysts

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Abstract

The preparation of heterogeneous catalysts has by now lost all empirical aspects. The approach is scientific and involves a wide number of specific competencies of solid state chemistry, analytical chemistry, physical chemistry, kinetics, rheology, etc. The fundamental aspects in the preparation of heterogeneous catalysts starting from catalyst design up to the catalyst in its final form are briefly reviewed, with focus on the key factors in each preparation step and the main differences between laboratory and industrial scale preparations. The main properties of monolithic catalysts and their preparation methods are also reported, considering their relevance for environmental applications.

Keywords: Heterogeneous catalysts; Catalyst design; Catalyst preparation; Unsupported catalysts; Supported catalysts; Hydrothermal treatments; Thermal treatments; Forming; Monolith catalysts; Preparation scale-up

1. Introduction

Heterogeneous catalysts are frequently defined as solids or mixtures of solids which accelerate chemical reaction without themselves undergoing changes. This definition however is too limited in scope, considering that the properties of catalysts can change significantly with use, with service lives that vary from minutes to years. The term “solid” has to be understood in its widest meaning [including, for example, liquid acid (sulphuric or phosphoric) impregnated on porous supports or catalysts containing mobile phases (for example, K-containing steam reforming catalysts)]. The overall chemical reactions concern the gas-phase species. The solid is involved in the formation of intermediate species and the influence of the solid does not effectively extend more than an atomic diameter into the gas phase. The direct involvement of atoms below the topmost layers is not usually possible.

For many years, the development and preparation of heterogeneous catalysts were considered more as alchemy than science [1], with the predominance of trial and error experiments. However, this approach is expensive, time-consuming, does not offer assurances on the final results and discourages osmosis between catalysis and other related sciences, such as analytical or solid state chemistry, spectroscopy, etc. Thus, it is not surprising that catalysis followed a solitary route up until the 1970s when the idea of scientific bases for the preparation of catalysts began to develop [2], with significant integration and overlapping between the different sciences. In this perspective a more appropriate term would be catalytic materials, i.e. not only catalysts, but also gas sensors, electronic devices, etc.

The wide number of variables in preparing heterogeneous catalysts can be reduced to a series of elementary steps, which present quite strongly marked analogies from one catalyst to another, and may be

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described in a general way. Many excellent reviews have already been published on the different topics, e.g. [3–16]. The present paper differs in its aim to offer a general overview devoted to young researchers, starting from the catalyst project, through the unit operations in the preparation and, finally, scale-up of the process. It must be noted that all these steps may not always be required, since a new catalyst may consist only of minor modifications of an existing catalyst and the preparation scale-up is not generally required in academic institutions. A wide ranging approach, however, is always necessary. All the preparation steps must be considered. Even though scale-up may not be required, for example, it has to be considered in the laboratory studies, so that the solution of many problems can be anticipated and routes impracticable on a larger scale are not pursued [6,11,16].

2. Catalyst design

The design of a catalyst covers all aspects from choice of the active phases to the method of forming particles. It can be rigorous and detailed, starting from fundamentals to get the best catalyst for a new process [8,9,12,14,15,17–20], however, in many cases the design of a new catalyst is only an improvement of an existing industrial catalyst. In any case, at the start of catalyst design consideration of desirable and undesirable reactions in the overall process as well as the fundamental properties and their mutual relationships in the different steps leads to the choice of the active species (Fig. 1). Suitable promoters are frequently added to obtain adequate performance. They may either modify the catalyst structure, so improving stability, or enhance the catalytic reactions to give better activity or selectivity. However, the nature of the active species is always the most important factor (Table 1).

Table 1
Effects of different parameters on the activity for some catalytic reactions [27][a]

Reaction	Role of		
	Metal structure	Promoters	Metal nature
$H_2 + D_2 \Rightarrow 2HD$	1–10	$10–10^2$	$10^2–10^4$
$C_2H_4 + H_2 \Rightarrow C_2H_6$	1–10	$10–10^2$	$10^2–10^4$
Cyclo-$C_3H_6 + H_2 \Rightarrow C_3H_8$	1–10	$10–10^2$	$10^2–10^4$
$C_6H_6 + 3H_2 \Rightarrow C_6H_{12}$	1–10	$10–10^2$	$10^2–10^4$
$C_2H_6 + H_2 \Rightarrow 2CH_4$	$10–10^2$	$10^4–10^6$	$>10^6$
$N_2 + 3H_2 \Rightarrow 2NH_3$	$10^2–10^4$	$10^4–10^6$	$>10^6$

[a] The order of magnitude of the effects is classified as follows: $1 <$ very small < 10; $10 <$ small $< 10^2$; $10^2 <$ medium $< 10^4$; $10^4 <$ large $< 10^6$; $10^6 <$ very large.

An heterogeneous catalyst is a composite material, characterised by: (a) the relative amounts of different components (active species, physical and/or chemical promoters, and supports); (b) shape; (c) size; (d) pore volume and distribution; (e) surface area. The

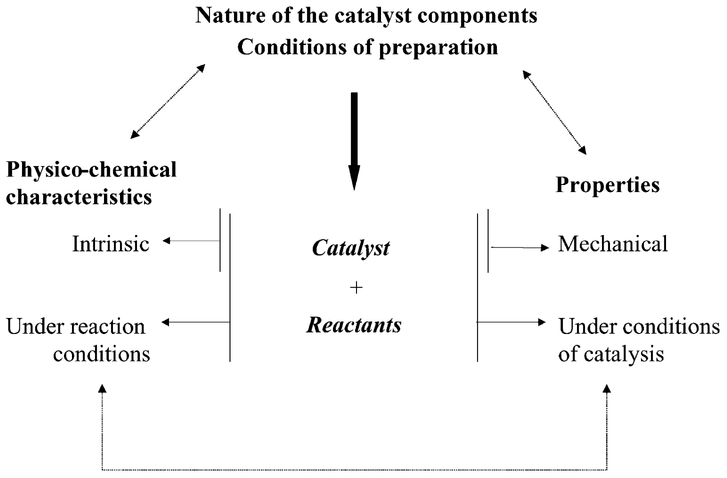

Fig. 1. Principal factors in catalysis and how they are interrelated [12,21].

optimum catalyst is the one that provides the necessary combination of properties (activity, selectivity, lifetime, ease of regeneration and toxicity) at an acceptable cost. These requirements are in many cases in conflict and catalyst design mainly consists of the achievement of a suitable compromise [12,22,23]. Today, many advantages are offered by combinatorial synthesis and rapid screening methods [24–26]. They allow the exploration of large and diverse compositional and parameter spaces by establishing an integrated workflow of rapid parallel and combinatorial synthesis of large numbers of catalytic materials, subsequent high-throughput assaying of these compounds and large-scale data analysis. Thus, the number of experiments that can be screened has risen by orders of magnitude, resulting in a much higher probability of discovering new catalysts or materials.

3. Catalyst preparation

The preparation of the catalysts can be reduced to a series of elementary steps, or unit operations, which present marked analogies and can be described in a general way [3–5,7,10,13,20–23,28,29]. For example, summarised in Fig. 2 are the main pathways and objectives in the preparation of unsupported catalysts, including both high-temperature and solution methods. Other examples may be considered such as the *unsupported metals*, which have very few industrial applications (for example, precious metal gauzes in the oxidation of ammonia or granules of agglomerated dendritic crystals of silver in the oxidation of methanol), where the purity of the reagents and the rate of the catalysed reaction are so high that a small metal area is sufficient [23]. Generally, the catalysts may be classified according to the preparation procedure as: (i) bulk catalysts or supports and (ii) impregnated catalysts. On this basis the relative preparation methods are: (i) the catalytic active phase is generated as a new solid phase and (ii) the active phase is introduced or fixed on a pre-existing solid by a process which intrinsically depends on the support surface.

3.1. Bulk catalysts

The first unit operation is to obtain a solid and, apart from a few examples of *fused catalysts* (promoted iron catalyst for ammonia or Fischer–Tropsch syntheses and Raney catalysts) [23,29,30], this is generally achieved by precipitation [4,10,13,20,22,23]. The aim of this step is to precipitate a solid from a liquid solution, as either a precipitate or gel. The precipitate or gel is generally a precursor, the nature of which determines the structure and properties of the final solid catalyst, that forms as a result of successive operations. The precursor may be a crystalline, a gel or a flocculate precipitate.

The *precipitation* of a crystalline solid can be divided into three steps: supersaturation, nucleation and growth. In the supersaturation region the system is unstable and precipitation occurs as a result of any

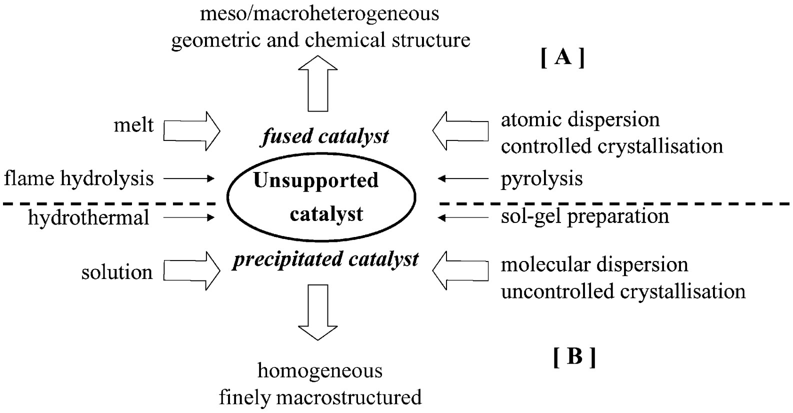

Fig. 2. Main pathways and objectives in the production of unsupported catalysts; the dashed line separates (A) high-temperature and (B) solution methods [29].

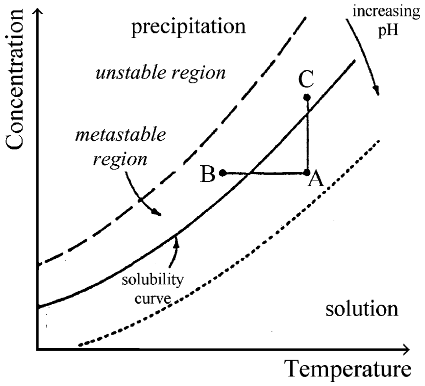

Fig. 3. Concentration as a function of temperature and pH during the precipitation step (pathways to increase the concentration: A → B decrease in temperature; A → C solvent evaporation) [10,22].

small perturbation (Fig. 3). Supersaturation is reached by means of physical transformations (change in temperature or solvent evaporation) or chemical processes (addition of bases or acids, use of complex forming agents). Formation of the solid phase occurs in two elementary steps: (i) nucleation, formation of the smallest elementary particles of the new phase which are stable under the precipitation conditions, and (ii) growth or agglomeration of the particles. Under conditions of high supersaturation the rate of nucleation is much higher than the rate of crystal growth and leads to the formation of numerous but small particles. In this condition amorphous precipitates can be obtained. [4,10,31].

Usually precipitates with specific properties are desired. These properties include the nature of the phase formed, chemical composition, purity, particle size, surface area, pore size, etc., as well as the requirements of downstream processes (drying, palletizing or calcination). Basically, all process parameters influence the quality of the final precipitates, and fine tuning of the parameters is necessary in order to produce the required material (Fig. 4). The chemical and physical properties of the precipitates in contact with their mother liquor may further change, due to hydrothermal phenomena (see next paragraph).

Precipitation is one of the most widely employed preparation methods and may be used to prepare either single component catalysts and supports or mixed catalysts, see for example: [4,10,13,20,22,23,31–33]. In the latter case intimate mixing of the catalyst components can be achieved by either the formation of very small crystallites or the formation of mixed crystallites containing the constituents. During coprecipitation the pH has to be adjusted and kept constant

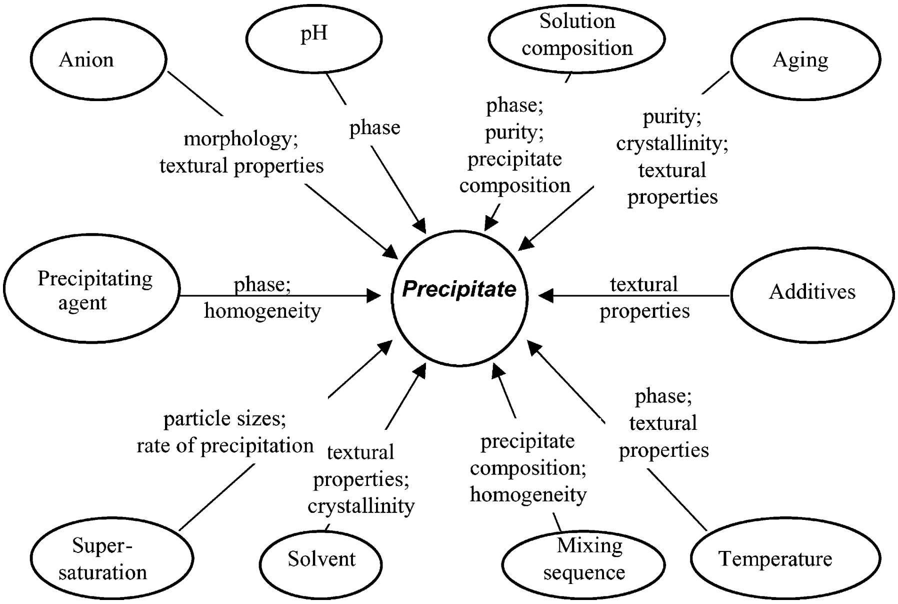

Fig. 4. Factors affecting the main properties of precipitated catalysts [31].

[4,31,32]. Hydroxides and carbonates are the preferred precipitates because of their low solubility, easy decomposition and minimal toxicity and environmental problems [23].

The *gelation route* (sol–gel method) is a homogeneous process which results in a continuous transformation of a solution into a hydrated solid precursor (hydrogel). Sol–gel methods have several promising advantages over precipitation. In general, sol–gel syntheses have been recognised for their versatility which allows better control of the texture, composition, homogeneity and structural properties of the final solids. The nanoscale chemistry involved in sol–gel methods is a more direct way to prepare highly divided materials [10,34]. Four main steps may be identified in taking a precursor to a particular product via sol–gel preparation: formation of a hydrogel, its ageing, removal of solvent and heat treatment (Fig. 5). The

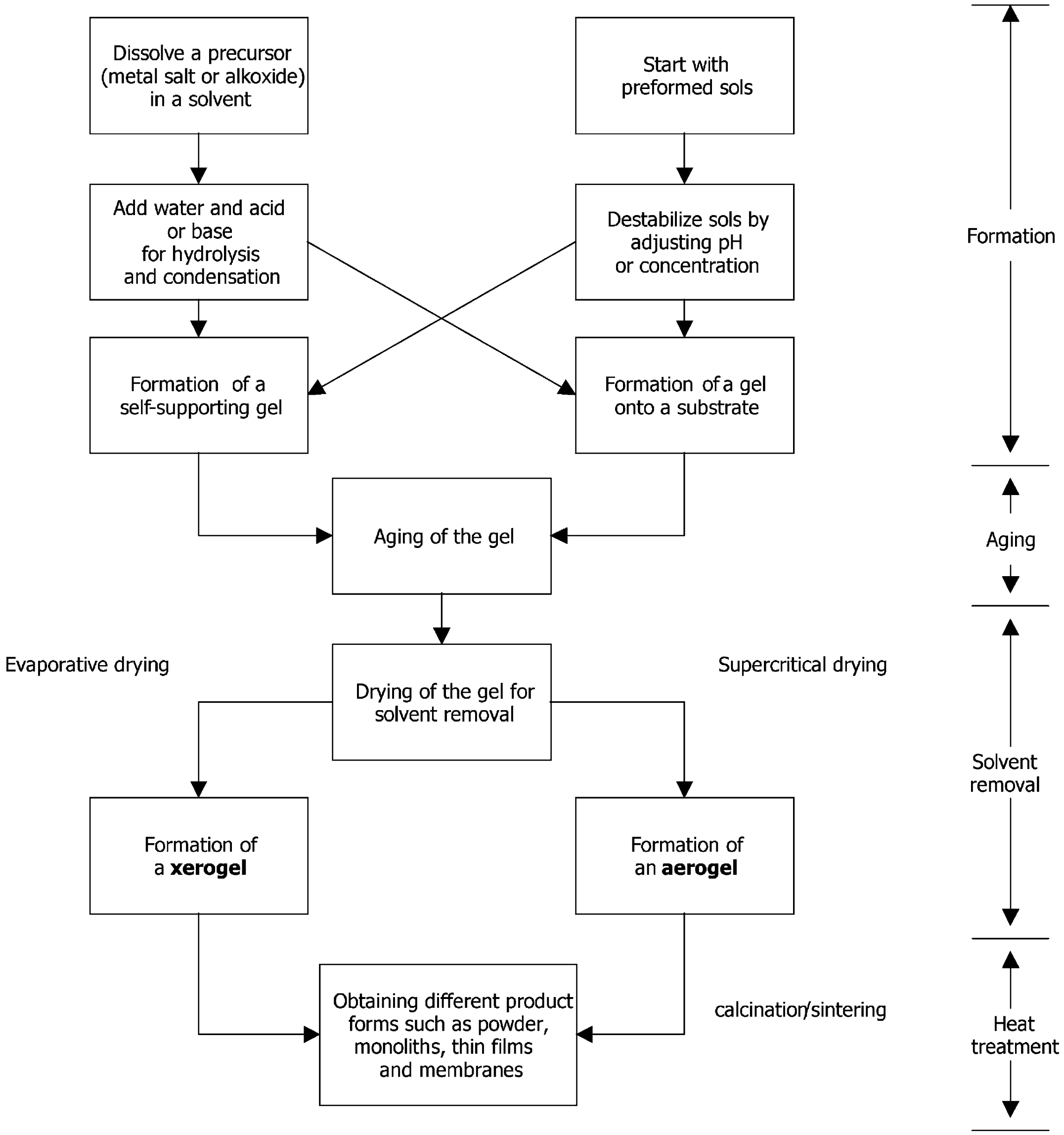

Fig. 5. Schematic diagram of the different steps in the sol–gel preparation [34].

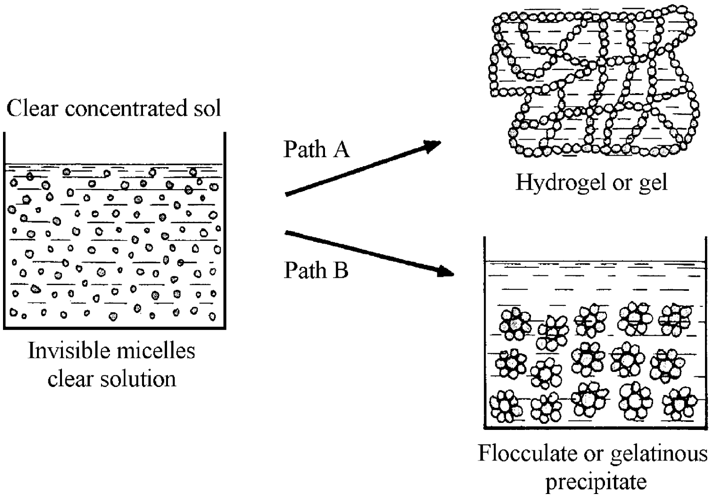

Fig. 6. Mechanism of the formation of gels (A) and flocculates (B) [10,20].

versatility of this preparation method lies in the number of parameters that can be manipulated in each of these steps [34].

Hydrophilic colloidal solutions are formed of micelles that remain separated because of electrical charges on their surface and in the surrounding solution. These charges create repelling forces which prohibit coagulation of the micelles. The point at which the hydrogel formation, called gelation, occurs depends on the micelle concentration, temperature, ionic strength of the solution and especially the pH. The chemistry of the processes can be represented by a sequence of acid- or base-catalysed nucleophilic additions or substitutions [hydrolysis (A) and condensation (B)].

- (A) $-\mathrm{M{-}OR} + \mathrm{H_2O} \Rightarrow -\mathrm{M{-}OH} + \mathrm{R{-}OH}$.
- (B) $-\mathrm{M{-}OH} + \mathrm{XO{-}M}- \Rightarrow -\mathrm{M{-}O{-}M}- + \mathrm{X{-}OH}$.

where X can be either H or an alkyl group R. However, this description oversimplifies the overall process because it does not represent the nature of the intermediates and end products, nor does it depict the simultaneous occurrence of the two reactions. Key factors are the relative rates of hydrolysis and condensation, due to their impact on the properties of the product [34,35].

The overall process produces a reticulate, metastable polymer with an open structure in which the primary units are held together by either chemical bonds, hydrogen bonds, dipole forces or van der Waals interactions. This framework includes almost all the solvent (Fig. 6, path A) [10,20]. The gelation time ranges from a few minutes to a 100 h and the density of the hydrogel increases with increasing concentration of the original salts in the solution and with the gelation rate. The homogeneity of the hydrogel depends on the solubility of the reagents in the solvent used, the sequence of addition of reactants, the temperature and the pH. Flocculation of a sol can be obtained through the neutralisation of the micelle charges and the flocculate precipitates more or less well. Hydrophilic sols give jelly-like flocculates that contain large amounts of water (Fig. 6, path B) [10,20]. The flocculates are denser than hydrogels and the elementary solid particles have the dimensions of the original micelles.

The surface area of the final solids depends on the original micelle size and also on the ripening and drying conditions. Due to the possibility of obtaining high-surface-area solids with homogeneous compositions and controlled porosity, sol–gel methods have been widely employed for the synthesis of micro and mesoporous materials [10,34,36–40], mixed oxides [41–43], layer double hydroxides [44,45], hydroxyapatite [46], composite powders [47], etc.

3.2. Supported catalysts

Supported catalysts consist of an active phase dispersed on a carrier [3,5,10,12,22,23]. The catalytic reaction takes place at the internal surface (i.e. in the pores) of the catalyst. Good supports combine relatively high dispersion with a high degree of thermal stability of the catalytic component [3,5,10,23]. Furthermore, the support should enable the production of a large shaped particle composed of very small easily sintered crystals of active phase which are prevented from coalescing by being separated by the support component. A detailed review on model supported catalysts and their properties for studies in fundamental catalysis has been published by Gunter et al. [48].

Pre-shaped supports are attractive because their texture, regulated in advance, is transmitted almost unchanged to the final catalyst. However care must be taken that dispersion of the catalytic components is not modified in the following steps. With powdered supports, the intimate mixing of deposition of the catalytic components is easily realised during the first step, however the following operations, in which the grains are transformed into their required shape and porosity, are more difficult and the dispersion may not be uniform. Wetting of the support with a solution or a slurry of the active phase precursors is the operation that characterises such preparation. The most common preparation methods are impregnation, ion-exchange, adsorption and deposition–precipitation [10,20,22,23,49–51].

Impregnation [10,20,23,49] is the procedure whereby a certain volume of solution containing the precursor of the active phase is contacted with the solid support, which, in a subsequent step, is dried to remove the imbibed solvent. Two methods of contacting may be distinguished, depending on the volume of solution: wet impregnation and incipient wetness impregnation. In *wet impregnation* (Fig. 7A) an excess of solution is used. After a certain time the solid is separated and the excess solvent is removed by drying. The composition of the batch solution will change and the release of debris can form a mud which makes it difficult to completely use the solution. The heat of adsorption is released in a short time. In *incipient wetness impregnation* (Fig. 7B) the volume of the solution of appropriate concentration is equal or slightly less than the pore volume of the support. Control of the operation must be rather precise and repeated applications of the solution may be necessary. The maximum loading is limited by the solubility of the precursor in the solution. For both methods the operating variable is the temperature, which influences both the precursor solubility and the solution viscosity and as a consequence the wetting time. The concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying.

Ion exchange [10,20,23,49] consists of replacing an ion in an electrostatic interaction with the surface of a support by another ion species [10,49]. The support containing ions A is plunged into an excess volume (compared to the pore volume) of a solution containing ions B. Ions B gradually penetrate into the pore space of the support, while ions A pass into the solution, until equilibrium is established corresponding to a given distribution of the two ions between the solid and the solution [49]. For example, using a proper salt solution at ca. 100 °C (to increase the exchange rate), it is possible to prepare the acid form of zeolite by exchanging NH_4^+ for Na^+ and successive calcination [52].

Adsorption [10,20,23,50] allows the controlled anchorage of a precursor (in an aqueous solution) on the support. The term adsorption is used to describe all processes where ionic species from aqueous solutions are attracted electrostatically by charged sites on a solid surface. Often consideration is not given to the difference between true ion exchange processes and electrostatic adsorption at the charged surface of oxides. Catalyst systems, which need charge compensating ions are ideal materials for ion exchange (zeolites, cationic clays or layered double hydroxides). Instead most oxide supports, when placed in an aqueous solution, develop a pH-dependent surface charge. These oxides may show a tendency for adsorption of cations (SiO_2–Al_2O_3, SiO_2), or anions (ZnO, MgO) or both, cations in basic solutions and anions in acid solutions (TiO_2, Al_2O_3). The surface charge of an oxide depends on its isoelectric point as well as on the pH and ionic strength of the solution.

In *deposition–precipitation* [3,5,10,20,23,51] two processes are involved: (1) precipitation from bulk solutions or from pore fluids; (2) interaction with the

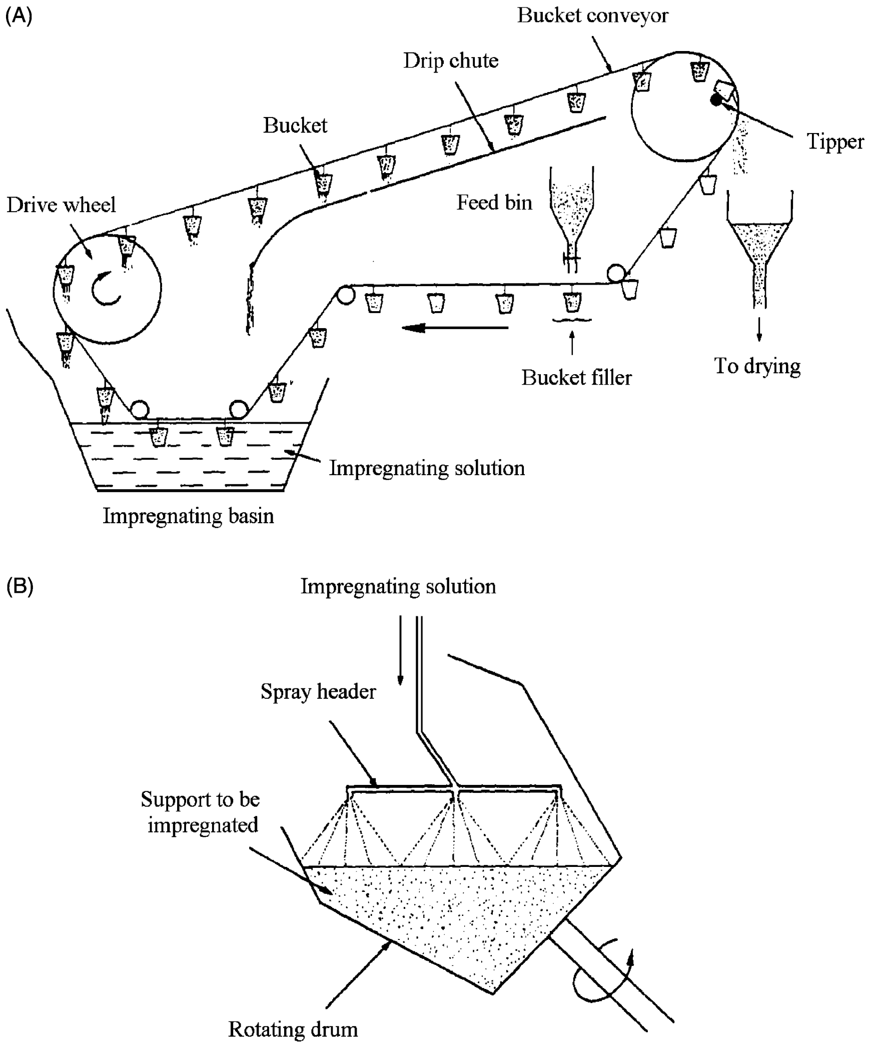

Fig. 7. Impregnation methods for the preparation of supported catalysts: (A) wet impregnation (with excess solution); (B) incipient wetness impregnation [10,20].

support surface. Slurries are formed using powders or particles of the required salt in amounts sufficient to give the desired loading, then enough alkali solution is added to cause precipitation. However, precipitation in the bulk solution must be avoided, since it gives rise to deposition outside the pores of the support. A well-dispersed and homogeneous active phase is reached when the OH^- groups of the support (for example, the silanols of silica) interact directly with the ions present in the solution, thereby also determining the nature of the phase formed [10,51,53]. The nucleation rate must be higher at the surface than in the bulk solution and the homogeneity of the solution must be preserved. A method to obtain uniform precipitation is to use the hydrolysis of urea as a source of OH^- instead of conventional alkali. Urea dissolves in water and decomposes slowly at ca. 90 °C., giving a uniform concentration of OH^- in both the bulk and pore solutions. Thus the precipitation occurs evenly over the support surface, making the use of urea the preferred method for amounts higher than 10–20%.

Table 2
Main hydrothermal transformations [10,20,54]

From	To
Amorphous solids	Crystalline solids
Small crystals	Large crystals
Small amorphous particles	Large amorphous particles
Kinetically favoured phases	Thermodynamically favoured phases
High porosity gels	Low porosity gels

4. Hydrothermal treatments

Hydrothermal treatments refer to treatments of precipitates, flocculates or gels carried out at rather low temperature ($<300\,^{\circ}$C), under ageing or ripening in the presence of the mother liquor [7,10,20,54].The variables in these types of operation for a given solid are pH, temperature, pressure, time and concentration. The main difference between ageing and hydrothermal treatments regards the reaction conditions (mainly T, P and time), ageing being performed at room temperature and pressure for longer times. A detailed study on the role of ageing on the formation of porous silica has been published by Beelen et al. [7]. All textural or structural hydrothermal transformations (Table 2) obey the thermodynamic laws and thus proceed toward a decrease in free energy of the system. Increasing interest has been devoted in the last decades to the synthesis of zeolites and mesoporous materials, in which the original amorphous gels crystallise in hydrothermal conditions around different templating agents [10,34,36–40,52,55]. Most hydrothermal treatments are performed in the presence of a liquid phase (mainly the mother liquor); however they also include the steam stabilisation procedure of Y zeolites [37,39,52,55].

5. Solid-phase recovery

Separation of the solid phase from the mother liquor can be performed by decantation, filtration and centrifugation, followed by washing with distilled water to remove completely the mother liquor and eliminate impurities [10,20]. The separation operations are easy for crystalline precipitates, difficult for flocculates and useless for hydrogels. Choice of the separation method depends on the particle size of the solids, since for example, small particles may require filtration or centrifugation. When washing flocculates, problems may arise since removal of counterions reverts flocculates to sol (peptization), thus care must be taken not to wash too much or allow the settling time to become too long.

6. Thermal evolution

The thermal treatments include drying, calcination (or heating) and activation [10,20,22,23]. *Drying* is the elimination of the solvent (usually water) from the pores of a solid. This is a routine procedure for crystalline solids but becomes critical for flocculates and even more so for hydrogels that contains up to 90% water [10,22]. In these latter cases, the removal of water can result in a collapse of the structure and drying has to be properly controlled if high porosity is desired. As a function of the procedure adopted to dry a hydrogel, the final solid may be called by different names: xerogels, aerogels, carbogels, etc. In air, initial drying takes place on the outside surface of the hydrogel and the mass transfer is controlled by temperature, relative humidity, flow rate of air over the surface and size of the gel particles. This process continues until the moisture content is reduced to ca. 50% and the solids so obtained are called xerogels [10]. The following step occurs with a declining rate, since evaporation is controlled by capillary forces. The saturation point decreases as pores becomes smaller and evaporation slows, but if removal of moisture is blocked by smaller pores, an internal pressure of steam develops and the structure collapses, with loss of pore volume and surface area. Gel breakage may be reduced by lowering the temperature gradient, increasing the relative humidity of the drying medium or decreasing the air flow through the gel bed [56]. Large capillary stresses can be avoided by removing the water: (1) under vacuum at temperatures ranging from -50 to $-5\,^{\circ}$C (lyophilisation) or operating at temperatures higher than the critical temperature of water [20]. However, since this temperature is too high, softer operating conditions can be obtained by replacing the water with alcohols (generally methanol) or liquid CO_2, and always operating at temperatures higher than their critical temperatures. The solid structure retains the textural properties of the wet gel and highly porous dry solids are obtained (aerogels or carbogels, respectively) [57].

Calcination means heating without the formation of a liquid phase and is a further heat-treatment beyond drying. It is carried out in air at temperatures higher than those used in the catalytic reaction or catalyst regeneration. When different atmospheres are employed (N_2, vacuum, etc.), the term *heating* is used rather than calcination. As with drying, this unit operation can be located before or after the forming operation. Finally, the term *activation* refers to other thermal treatments, such as *reduction* or *sulfidation*, performed in special atmospheres usually in the reactor at the start-up of the unit. Therefore, activation is not considered strictly to be a preparation procedure. Several processes occur during calcination or heating: loss of chemically bonded H_2O or CO_2, modification of the nature and/or structure of the phases present, generation of the active phase and stabilisation of mechanical properties, and texture modification through *sintering* (sintering is the formation of larger particles from small crystals or particles without the formation of a liquid phase and consequently results in the loss of surface area and pore volume). The heating temperature and atmosphere must be properly chosen to obtain phases that are stable in the reaction and regeneration conditions, at the same time avoiding sintering phenomena as much as possible, since they have a negative effect on the catalytic performance. A substance which inhibits sintering is called a textural or physical *promoter* [58].

Calcining xerogels can result in various types of sintering which range from: (i) sintering at constant pore radius, with reduction in the total pore volume, typical of xerogels with covalent bonds (for example, silica and silica alumina) to (ii) sintering at constant pore volume, with an increase in the pore sizes, typical of xerogels with ionic bonds (for example, ferric hydroxide) [10,20]. An intermediate case between these two extremes is, for example, that of sintering at constant pore volume which results from heating a xerogel with covalent bonds in the presence of steam.

7. Forming operations

Although in many cases not sufficiently considered in the lab-scale tests, the shaping of catalysts and supports is a key step in the catalyst preparation procedure. The shape and size of the catalyst particles should promote catalytic activity, strengthen the particle resistance to crushing and abrasion, minimise the bed pressure drop, lessen fabrication costs and distribute dust build-up uniformly [10,20,23,59]. Unfortunately, several of these objectives are mutually exclusive. For example, small particle size increases activity, but also increases bed pressure drop. Thus, the best operational catalysts have the shape and size that represent an optimum economic trade-off [60]. The choice of the shape and size is mainly driven by the type of reactor (Table 3). Moreover, for a given reactor the best shape and size of the catalyst particles depend on the hydrodynamics and heat and mass transfer limitations (Table 4).

Table 3
Different catalyst shapes [10,59]

Shape	Size	Reactor type
Microspheres	$d = 20–100\,\mu m$	Fluid bed reactor, slurry reactor
Spheres	$d = 1–10\,mm$	Fixed bed reactor, moving bed reactor
Granules	$d = 1–20\,mm$	Fixed bed reactor
Beads	$d = 1–5\,mm$	
Pellets	$d = 3–15\,mm$, $h = 3–15\,mm$	Fixed bed reactor
Extrudates	$d = 1–50\,mm$, $l = 3–30\,mm$	Fixed bed reactor

Table 4
Criteria for choosing the catalyst particle size and shape [10,23]

Reactor	Problem	Best shape
Fluid bed	Poor fines recovery by cyclones	Larger spheres
	Poor bed fluidisation	Smaller spheres
Slurry	Difficult filtration	Larger particles
	Poor suspension	Smaller particles
Fixed bed	Large internal diffusion phenomena	Extrudates (ring, star, granule)
	Cost	Extrudates
	Pressure drop	Large size and not regular shape
	Poisons in the feed	Extrudates (large external area)
	High pressure on bottom layer	Pellets (regular shape)
	Charging height or catalytic bed movements	Pellets (regular shape)

Crushing and grinding of calcined solids are useless to produce *microgranules*, since the powder obtained has a broad particle size distribution, with a lower limit of a few microns, and poor mechanical resistance [10,20,22,23]. To produce microspherical materials (<1 mm) spray drying is a suitable technique, in which a sol or a hydrogel is injected through nozzles into a heated zone. Important process parameters are the viscosity of the liquid, the solid content of the suspension, the film-forming characteristics, the type of atomiser, the temperature and the gas velocity [10].

Granules are particles with a more or less spherical shape and diameter ranging from 1 to 20 mm [10,20,22,23]. To prepare them a round dish rotating on an inclined axis is used (snowball effect). Small particles are fed into the dish, while a cohesive slurry is contemporaneously sprayed on them. The slurry sometimes also contains some binder and cement to favour the layer adhesion. The particle surface becomes wet and rotating granules grow, developing layer by layer into larger, more or less spherical particles. After drying, the spheres are calcined to obtain high mechanical strength. Spheres with a similar size range may also be obtained by drop coagulation from sols by simultaneous gelation, ripening and forming. The aqueous sol is forced through a sparger in a water-immiscible solvent, the temperature of which is raised to ca. 100 °C (sometimes the pH is also increased). The surface tension created on the droplets gives rise to the formation of gel spheres that are then ripened and dried. During drying contraction of the bead without deterioration is observed as long as the diameter is not too large.

Extrusion is the most economic and commonly applied shaping technique for catalysts and supports [10,20,22,23]. A wet paste is forced through a die and the emerging ribbon is cut to the desired length using a suitable device. Usually the catalyst powders obtained after the thermal treatments behave like sand, i.e. do not have by themselves the required mouldability and plasticity, even when water is added. Various additives are used in formulation of the paste: (i) compounds for improving the rheological behaviour (clays or starch); (ii) binders (aluminas or clays); (iii) peptizing agents to deagglomerate the particles (dilute acetic or nitric acid); and (iv) combustible materials to increase the porosity (carbon black, starch, etc.). The operating variables include mixing time, additive content, water content, ageing, and extrusion temperature. The quality of the extrudates also depends on the drying and calcination procedure. Special shapes (trilobates, rings, hollow cylinders, monoliths or honeycombs) can be obtained using proper dies.

Pellets are obtained by dry tableting, in which a dry powder is pressed between two punches in a press [10,20,22,23]. The production of strong pellets requires that the fed particles are subjected to an almost uniform triaxial pressure and that under this pressure they are crushed together to form a dense bed which then welds at contact points. At the tableting stresses generated by industrial machines, the requirement of welding implies that a sufficient fraction of the material has adequate ductility. A very crude relationship exists between ductility, melting point, elastic modulus and Mohs scale of hardness (Fig. 8) [61]. Lubricants (mineral oil, talc, graphite, stearates, etc.) and binders (aluminas, clays, etc.) can be added to achieve the proper qualities. Compared to other shaping methods tableting is quite an expensive method. It is very useful however in lab-tests to prepare samples for fixed-bed microreactor tests, starting from the calcined powders. The pellets are then crushed and sieved to the suitable particle size (reactor diameter/particle size ca. ≥10).

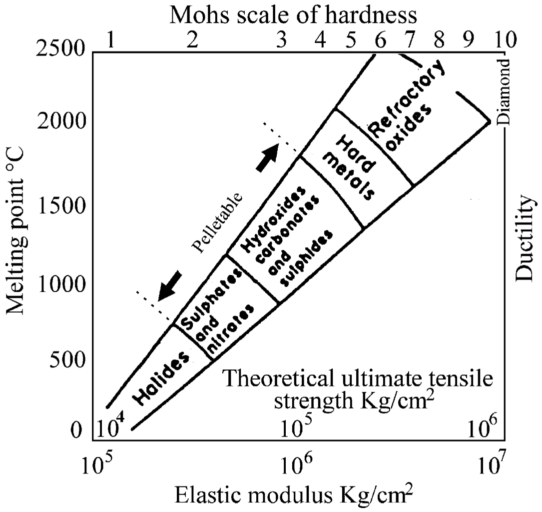

Fig. 8. Relationship between ductility, melting point, elastic modulus and Mohs scale of hardness [10,61].

8. Monolithic catalysts

Monolith comes from the Greek “mono lithos” (single stone) and monolithic catalysts are well known from environmental applications, although further promising large-scale applications are foreseen in multiphase processes, in which monolithic catalysts compare favourably to slurry and trickle bed catalysts, or in particularly fast reactions at high temperatures (steam reforming, partial oxidation of hydrocarbons to synthesis gas, oxidative dehydrogenation, etc.) [62–64]. Since the catalyst consists of one piece, no attrition due to moving particles in a vibrating case occurs. Furthermore, the large, open frontal area giving access to straight channels results in an extremely low pressure drop and prevents the accumulation of dust. However, monoliths also have some disadvantages, the major ones being laminar flow through the channels, lack of interconnectivity between the channels, and poor radial heat conductivity. A laminar flow profile yields a large residence time distribution, which is unfavourable for high conversion levels. Although the only radial transport is the diffusion of fluid phase reactants to the walls of the monolith channels, due to the small channels and high gas diffusivity, this radial transport is sufficiently fast. On the contrary, in the liquid phase the diffusivity is three orders of magnitude lower and this may be one of the reasons why monoliths are not widely popular for liquid phase reactions [64].

Despite the many applications of monolithic catalysts, few papers describe their preparation in some detail [62,64–69], probably because most preparation work is done by industries and commercial interest in publishing the progress achieved is scarce. Ceramic monoliths can be manufactured by extrusion or by corrugation, the former being the technique mainly used and employing various materials, although cordierite or mullite are most often used especially as catalyst supports [62,65,66]. On the contrary, metallic monoliths are produced exclusively by corrugation, followed by rolling up or folding into monoliths of the shape and size required [65]. The disadvantage of ceramic monoliths is their low thermal conductivity, which excludes them from applications where heat exchange with the surroundings through their walls is needed. In extrusion, in addition to the nature and the properties of the materials used to make the mouldable mixture, the additives used, the pH, the water content, and the force used in extrusion are also of importance in determining the monolith properties [70].

There are two basic types of monolith catalysts: (i) incorporated type catalysts, (ii) coated-type catalysts (Fig. 9). *Incorporation* of catalytic components into the monolith is performed by adding them to the ingredient mixture from which the monolith is to be subsequently formed and calcined. Calcination requires special care because of the possible reaction of the active phase with the monolith matrix or the atmosphere. A characteristic of such catalysts is that a significant amount of active component is located deep in the matrix, making the diffusion path to active sites longer and decreasing their accessibility to the reactants.

Catalytic compounds can also be deposited on the surface of the monolith, directly or via an intermediate step called washcoating. In both cases, the formation of a strong bond between the support and the active phase is a key factor. High-surface-area monoliths can be impregnated directly in such a way that pelleted catalysts are produced, dispersing the active sites more or less evenly throughout the walls of the monolith. Since the walls are ca. 10 times thicker than the washcoat layers of low-surface-area monoliths, this lengthens the path of the reactants at least to part of the catalytic surface. Although it is possible to extrude porous materials, leading to high-surface-area structures, calcination is essential in the production process and, as a consequence, sintering takes place, reducing the surface area. When a low calcination temperature is employed to preserve a high surface area, a mechanically weak structure results.

Washcoating consists of depositing a layer of high-surface-area oxide(s) onto the surface of a low-surface-area monolithic support and is by far the most used technique for both metallic and ceramic monoliths [65,71–75]. Active elements can be incorporated into the layer either during the washcoating step or after the washcoat has been deposited, using any well-known technique (impregnation, adsorption or ion exchange, precipitation or coprecipitation, deposition precipitation, sol–gel, slurry dip-coating and *in situ* crystallisation). Finally, many advanced techniques are available in the ceramic industry to coat a solid layer onto a solid surface or to make ceramic materials with special properties (spin-coating, chemical vapour deposition, chemical vapour infiltration, thermal spraying,

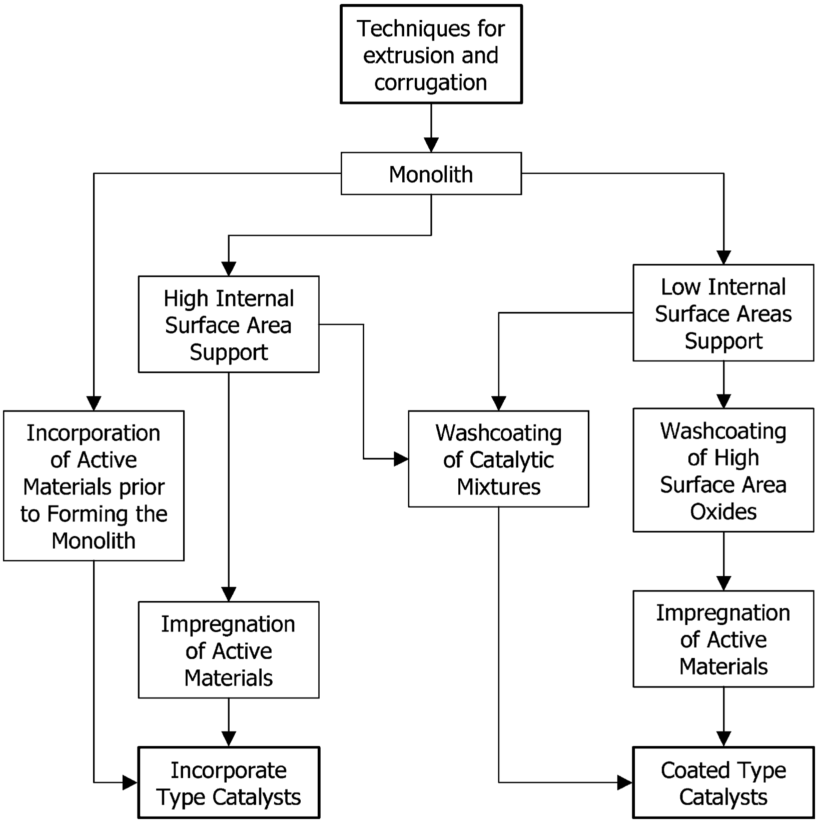

Fig. 9. Schematic diagram illustrating the preparation of monolith catalysts [62].

spray-coating, etc.) [65]. Some of these techniques may be applied to coat a solid layer on monoliths, provided suitable reactions and appropriate reaction conditions are chosen.

9. Catalyst scale-up

Frequently little consideration is directed towards this aspect in academic laboratories, however, when a catalyst preparation starts to be investigated with the goal of a possible industrial application, some attention should be devoted to its scaling-up in order to avoid useless reagents and/or preparation procedures [6,11,12,16]. The first aspect that should be studied is the role of reagent purity, since analytical reagents are usually employed in the laboratory while on a production scale technical grade reagents are employed. Also the different preparation unit operations may offer unpleasant surprises. For example, scale-up for precipitation would seem to be straightforward, but in practice difficulties may arise due to temperature and pH gradients, stirring geometry and connected geometry of precipitate formation, ageing time, etc. Additional problems can be found in large scale operations in the

Table 5
Classification of the preparation steps as a function of possible scale-up, from the lab-scale to industrial production [6,11,16]

Without scale-up problems	With scale-up problems
Hydrothermal or ageing treatments	Reagent purity grade
Solid recovery (filtration, sedimentation, centrifugation, etc.)	Mixing (concentration gradients, thermal gradients, pH control)
Washing	Thermal evolution (atmosphere control)
Drying	Forming
Activation	Poisoning or ageing

case of mixed coprecipitates, as a function of mixing procedure. Other critical points may be the thermal treatments, mainly calcination, for which industrially lack of homogeneity in the catalyst temperature and local gaseous atmosphere are very likely, even in gas-circulated ovens. Finally, since direct-flame heating is used for $T > 500\,^{\circ}\mathrm{C}$, the effect of the specific gas atmosphere must be checked (Table 5).

10. Conclusions and prospects

Although the development of heterogeneous catalysts has previously been treated in detail [8,76], at the end of this overview, it may be useful to briefly summarise the main advances achieved and the challenges that remain. It should be noted that currently the preparation of heterogeneous catalysts is almost totally approached on scientific bases, exploiting knowledge derived from other related sciences. For example, in the period 1967–1993, the number of papers and patents present in the literature dealing with catalyst preparation increased about two times (but that of patents remained almost constant). Even more impressive is the increase in papers dealing with catalyst characterisation [49]. This increase is even more dramatic if the most recent years are considered. A second relevant point is that key concepts, such as those of environmental catalysis and tailor-made catalysts, are today widely accepted. However, an evolution also occurred in these cases. For example, environmental catalysis refers currently not only to waste or pollution cleanup (secondary prevention), but also to pollution reduction or avoidance (primary prevention). Many examples of new and ecofriendly syntheses or processes based on tailor-made heterogeneous catalysts have been reviewed recently in the literature [77–87].

Heterogeneous catalysis is indeed a field where new challenges appear continuously, more and more charming and intriguing. Together with the continuous improvement in the area of the preparation of catalysts tailored for specific reactions and/or processes, mention also should be made of the impressive increase in the application of computational methods for the preparation, characterisation and testing of heterogeneous catalysts, which will facilitate the discovery of new catalyst compositions and applications. Furthermore, recently new "classes" of heterogeneous catalysts have also been developed. A few examples, without any presumption of being exhaustive include catalytic fibres or cloths [88], biomimetic catalysts [89], catalytic membranes [90], catalysts to operate in supercritical conditions [91] and heterogeneous enantioselective catalysts [14,92,93]. This list is certainly only partial and, furthermore, it can be expected that in the future many even more interesting catalysts and applications will appear in new and unexpected areas.

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References

[1] S.P.S. Andrew, CHEMTECH 9 (1979) 180.
[2] B. Delmon, P. Jacobs, G. Poncelet (Eds.), Preparation of Catalyst 1, Studies in Surface Science and Catalysis, vol. 1, Elsevier, Amsterdam, 1976, and following books of the same series (last vol. 143).
[3] J.W. Geus, in: G. Poncelet, P. Grange, P.A. Jacobs (Eds.), Preparation of Catalysts III, Studies in Surface Science and Catalysis, vol. 16, Elsevier, Amsterdam, 1983, p. 1.
[4] Ph. Courty, Ch. Marcilly, in: G. Poncelet, P. Grange, P.A. Jacobs (Eds.), Preparation of Catalysts III, Studies in Surface Science and Catalysis, vol. 16, Elsevier, Amsterdam, 1983, p. 485.
[5] P.T. Cardew, R.J. Davey, P. Ellitt, A.W. Nienow, J.P. Winterbottom, in: B. Delmon, P. Grange, P.A. Jacobs, G. Poncelet (Eds.), Preparation of Catalysts IV, Studies in Surface Science and Catalysis, vol. 31, Elsevier, Amsterdam, 1987, p. 15.
[6] I. Biay, C. Dessalces, C. Hypolite, F. Kolenda, J.P. Reymond, in: G. Poncelet, P.A. Jacobs, P. Grange, B. Delmon (Eds.), Preparation of Catalysts V, Studies in Surface Science and Catalysis, vol. 63, Elsevier, Amsterdam, 1991, p. 1.
[7] T.P.M. Beelen, W.H. Dokter, H.T. van Garderen, R.A. van Santen, E. Pantos, in: G. Poncelet, J. Martens, B. Delmon, P.A. Jacobs, P. Grange (Eds.), Preparation of Catalysts VI, Studies in Surface Science and Catalysis, vol. 91, Elsevier, Amsterdam, 1995, p. 33.
[8] I.A. Maxwell, in: J.W. Hightower, W.N. Delgass, E. Iglesia, A.T. Bell (Eds.), Proceedings of the 11th International Congress on Catalysis, Studies in Surface Science and Catalysis, vol. 101, Elsevier, Amsterdam, 1996, p. 1.
[9] A. Baiker, in: J.W. Hightower, W.N. Delgass, E. Iglesia, A.T. Bell (Eds.), Proceedings of the 11th International Congress

on Catalysis, Studies in Surface Science and Catalysis, vol. 101A, Elsevier, Amsterdam, 1996, p. 51.
[10] C. Perego, P.L. Villa, Catal. Today 34 (1997) 281.
[11] N. Pernicone, Catal. Today 34 (1997) 535.
[12] J.F. LePage, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley/VCH, New York/Weinheim, 1997, p. 49.
[13] A. Vaccari, Catal. Today 41 (1998) 53.
[14] G.J. Hutchings, D. Bethell, N. McGuire, P.C. Bulman Page, D. Robinson, D.J. Willock, F. Hancock, F. King, Curr. Top. Catal. 2 (1999) 39.
[15] M.E. Davies, in: A. Corma, F.V. Melo, S. Mendorioz, J.L.G. Fierro (Eds.), Proceedings of the 12th International Congress on Catalysis, Studies in Surface Science and Catalysis, vol. 130A, Elsevier, Amsterdam, 2000, p. 49.
[16] K. Johansen, in: E. Gaigneaux, D.E. De Vos, P. Grange, P.A. Jacobs, J.A. Martens, P. Ruiz, G. Poncelet (Eds.), Scientific Bases for the Preparation of Heterogeneous Catalysts Studies in Surface Science and Catalysis, vol. 143, Elsevier, Amsterdam, 2002, p. 1.
[17] D.A. Dowden, C.R. Schnell, G.T. Walker, in: Proceedings of the Fourth International Congress on Catalysis, vol. 2, Akademiai Kiado, Budapest, 1971, p. 201.
[18] D.A. Dowden, Chim. Ind. (Milan) 55 (1973) 639.
[19] D.L. Trimm, in: B. Delmon, P. Jacobs, G. Poncelet (Eds.), Preparation of Catalyst 1, Elsevier, Amsterdam, 1976, p. 1.
[20] J.-F. Le Page, J. Cosyns, P. Courty, E. Freund, J.-P. Franck, Y. Jacquin, B. Juguin, C. Marcilly, G. Martino, J. Miquel, R. Montarnal, A. Sugier, H. Van Landeghem, Applied Heterogeneous Catalysis: Design, Manufacture, Use of Solid Catalysts, Technip, Paris, 1987.
[21] R. Montarnal, J.F. La Page, La Catalyse au Laboratoire et Dans L'industrie, Masson, Paris, 1967, p. 231.
[22] J.T. Richardson, Principles of Catalyst Development, Plenum Press, New York, 1989.
[23] M.V. Twigg (Ed.), Catalyst Handbook, 2nd ed., Wolfe, London, 1989.
[24] R. Dagani, Chem. Eng. News 77 (10) (1999) 51.
[25] A. Hegemeyer, B. Jandeleit, Y. Liu, D.M. Poojary, H.W. Turner, A.F. Volpe Jr., W.H. Weinberg, Appl. Catal. A 221 (2001) 23.
[26] O.V. Buyevskaya, A. Brückner, E.V. Kondratenko, D. Wolf, M. Baerns, Catal. Today 67 (2001) 369.
[27] M. Boudart, M.A. McDonald, J. Phys. Chem. 88 (1984) 2185.
[28] J.M. Schwarz, C. Contescu, A. Contescu, Chem. Rev. 95 (1995) 477.
[29] R. Schlögl, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley/VCH, New York/Weinheim, 1997, p. 54.
[30] E. Lieber, F.L. Morritz, Adv. Catal. 5 (1953) 417.
[31] F. Schüth, K. Unger, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley/VCH, New York/Weinheim, 1997, p. 72.
[32] F. Cavani, F. Trifirò, A. Vaccari, Catal. Today 11 (1991) 173.
[33] F. Trifirò, A. Vaccari, in: J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vögtle (Eds.), Comprehensive Supramolecular Chemistry, vol. 7, Pergamon Press, Oxford, 1996, p. 251.
[34] E.I. Ko, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley/VCH, New York/Weinheim, 1997, p. 86.
[35] J. Livage, M. Henry, C. Sanchez, Prog. Solid State Chem. 18 (1988) 259.
[36] P.A. Jacobs, H.K. Beyer, J. Valyon, Zeolites 1 (1981) 161.
[37] A. Corma, Chem. Rev. 95 (1995) 559.
[38] X.S. Zhao, G.Q. Lu, G.J. Millar, Ind. Eng. Chem. Res. 35 (1996) 2075.
[39] A. Corma, Chem. Rev. 97 (1997) 2373.
[40] S. Biz, M.L. Occelli, Catal. Rev.-Sci. Eng. 40 (1998) 329.
[41] C. Beck, T. Mallat, T. Bürgi, A. Beiker, J. Catal. 204 (2001) 428.
[42] E.Y. Kaneko, S.H. Pulcinelli, V. Teixeira da Silva, C.V. Santilli, Appl. Catal. A 235 (2002) 71.
[43] B. Heinrichs, S. Lambert, C. Alié, J.P. Pirard, G. Beketov, V. Nehasil, K. Kruse, in: E. Gaigneaux, D.E. De Vos, P. Grange, P.A. Jacobs, J.A. Martens, P. Ruiz, G. Poncelet (Eds.), Scientific Bases for the Preparation of Heterogeneous Catalysts, Studies in Surface Science and Catalysis, vol. 143, Elsevier, Amsterdam, 2002, p. 25.
[44] T. Lopez, P. Bosch, E. Ramos, R. Gomez, O. Novaro, D. Acosta, F. Figueras, Langmuir 12 (1996) 189.
[45] F. Prinetto, G. Ghiotti, P. Graffin, D. Tichit, Microporous Mesoporous Mater. 39 (2000) 229.
[46] D.-M. Liu, T. Troczynski, W.J. Tseng, Biomaterials 22 (2001) 1721.
[47] N.N. Ghosh, P. Pramanik, Mater. Sci. Eng. C 16 (2001) 113.
[48] P.L. Gunter, J.W. Niemantsverdriet, F.H. Ribeiro, G.A. Samorjai, Catal. Rev.-Sci. Eng. 39 (1997) 77.
[49] M. Che, O. Clause, Ch. Marcilly, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley/VCH, New York/Weinheim, 1997, p. 191.
[50] H. Knözinger, E. Taglauer, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley/VCH, New York/Weinheim, 1997, p. 216.
[51] J.W. Geus, J. Van Dillen, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley/VCH, New York/Weinheim, 1997, p. 240.
[52] S. Bhatia, Zeolite Catalysts: Principles and Applications, CRC Press, Boca Raton, FL, 1990.
[53] L.A.M. Hermans, J.W. Geus, in: B. Delmon, P. Grange, P.A. Jacobs, G. Poncelet (Eds.), Preparation of Catalysts II, Studies in Surface Science and Catalysis, vol. 3, Elsevier, Amsterdam, 1979, p. 113.
[54] L.L. Henck, J.K. West, Chem. Rev. 90 (1990) 33.
[55] S.L. Suib, Chem. Rev. 93 (1993) 803.
[56] M.E. Winyall, in: B.E. Leach (Ed.), Applied Industrial Catalysis, vol. 3, Academic Press, New York, 1984, p. 43.
[57] G.M. Pajonk, Appl. Catal. 72 (1991) 217.
[58] C.N. Satterfield, Heterogeneous Catalysis in Practice, McGraw-Hill, New York, 1980, Chapter 4.
[59] E.B.M. Doesburg, J.H.C. van Hooff, in: J.A. Moullijn, P.W.N.M. van Leeuven, R.A. van Santen (Eds.), Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis, Studies in Surface Science and Catalysis, vol. 79, Elsevier, Amsterdam, 1993, Chapter 8.

[60] J.W. Fulton, Chem. Eng. 12 (1986) 97.
[61] S.P.S. Andrew, Chem. Eng. Sci. 36 (1981) 1431.
[62] A. Cybulsky, J.A. Moulijn, Catal. Rev.-Sci. Eng. 36 (1994) 179.
[63] M.C. Huff, Industrial Catalysis News 98 (6) (1998) 12.
[64] F. Kapteijn, J.J. Heisvwolf, T.A. Xander Nijhuis, J.A. Moulijn, CATTECH 3 (1) (1999) 24.
[65] X. Xu, J.A. Moulijn, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysis and Reactors, Marcel Dekker, New York, 1998, p. 599.
[66] J.P. De Luca, L.E. Campbell, in: J.J. Burton, R.L. Garten (Eds.), Advanced Materials in Catalysis, Academic Press, London, 1977, p. 293.
[67] I.M. Lachman, R.N. McNally, Chem. Eng. Prog. 81 (1985) 29.
[68] A.B. Stiles, Catalyst Supports and Supported Catalysts, Theoretical and Applied Concepts, Buttherworths, Boston, 1987, p. 6.
[69] S. Irandoust, B. Andersson, Catal. Rev.-Sci. Eng. 30 (1988) 341.
[70] G.J. Piderit, P.F. Toro, E. Cordova, in: Proceedings of the III Iberoam. Simp. Ceram. Vidrios Refract., vol. 2, Ass. Brasil. Ceram., Rio de Janeiro, Brazil, 1991, p. 631.
[71] X. Xu, H. Vonk, A. Cibulski, J.A. Moulijn, in: G. Poncelet, J. Martens, B. Delmon, P.A. Jacobs, P. Grange (Eds.), Preparation of Catalysts VI, Studies in Surface Science and Catalysis, vol. 91, Elsevier, Amsterdam, 1995, p. 1069.
[72] W.B. Kolb, A.A. Papadimitriou, R.L. Cerro, D.D. Leavitt, J.C. Summers, Chem. Eng. Prog. 89 (1993) 61.
[73] Y. Mizushima, M. Hori, Japanese Patent 0 543 344 (1993).
[74] R.D. Gonzalez, in: Proceedings of the AIChE Ann. Meeting, Miami Beach, FL, 1992, Paper 46f.
[75] K. Balakrishnan, R.D. Gonzalez, in: Proceedings of the AIChE Ann. Meeting, Miami Beach, FL, 1992, Paper 49a.
[76] H. Heinemann, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley/VCH, New York/Weinheim, 1997, p. 34.
[77] A. Corma, H. Garcia, Catal. Today 38 (1997) 257.
[78] A. Vaccari, Appl. Clay Sci. 14 (1999) 161.
[79] R.A. Sheldon, R.S. Downing, Appl. Catal. A 189 (1999) 163.
[80] J.M. Fraile, J.I. Garcia, J.A. Mayoral, Catal. Today 57 (2000) 3.
[81] M. Campanati, A. Vaccari, in: R. Sheldon, H. van Bekkum (Eds.), Fine Chemicals Through Heterogeneous Catalysis, VCH, Weinheim, 2000, p. 61.
[82] B.M. Choudary, M. Lakshmi Kantam, P. Lakshmi Santhi, Catal. Today 57 (2001) 17.
[83] B.F. Sels, D.E. De Vos, P.A. Jacobs, Catal. Rev. 43 (2001) 443.
[84] F. Basile, A. Vaccari, in: V. Rives (Ed.), Layered Double Hydroxides: Present and Future, Nova Science, New York, 2001, p. 285.
[85] A. Puzari, J.B. Baruah, J. Mol. Catal. A 187 (2002) 149.
[86] A. Mitsutani, Catal. Today 73 (2002) 57.
[87] C. Perego, P. Ingallina, Catal. Today 73 (2002) 3.
[88] Yu. Matatov-Meytal, M. Seituch, Appl. Catal. A 231 (2002) 1.
[89] D. De Vos, B.F. Sels, P.A. Jacobs, CATTECH 6 (2002) 14.
[90] P.E. Højlund Nielsen, B.S. Clausen (Eds.), Catal. Today 56 (2000) 1.
[91] A. Beiker, Chem. Rev. 99 (1999) 453.
[92] S.K. Tanielyan, R.L. Augustine, US Patent 6, 025, 295 (2000), Seton Hall University.
[93] A. Beiker, J. Mol. Catal. A 163 (2002) 205.