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Chapter 3

Catalyst preparation methods

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1. Introduction

Solid catalysts are highly sophisticated products derived from chemicals by means of several different procedures.

The catalytic properties of heterogeneous catalysts are strongly affected by every step of the preparation together with the quality of the raw materials. The choice of a laboratory method for preparing a given catalyst depends on the physical and chemical characteristics desired in the final composition. It is easily understood that the preparation methods are also dependent on the choice of the base materials and experience shows that several ways of preparation can be considered, even for a given selection of the base material.

This variety of possibilities might seem to confirm that making a catalyst is a 'black art' [1]. In the recent past, however, some generalities have become discernible in catalyst preparation and it may now be claimed that a catalyst preparation science is being built.

Despite the variety of possibilities of preparing catalysts we must consider that most of them can be reduced to a series of elementary steps, or unit operations, which present quite strongly marked analogies from one catalyst to another, and may therefore be described in a general way.

Such unit operations can be classified by:

(1) The chemical and physical transformations which are implied.

(2) The scientific laws which govern such transformations based on fundamental inorganic chemistry.

(3) The operation variables such as temperature, pressure, pH, time, concentration.

(4) The general characteristics of the products of the operation.

(5) The type of the required apparatus.

Table 1 reports the main unit operations usually applied in catalyst preparation, according to [2].

Most catalyst formulations involve a combination of some or even all these operations. However, even though the preparation procedures differ considerably from one catalyst to another, three broad categories can be introduced to classify the catalysts with respect to the preparation procedure:

1. Bulk catalysts and supports;
2. Impregnated catalysts;
3. Mixed-agglomerated catalysts.

Bulk catalysts are mainly comprised of active substances. Important examples include silica-alumina for hydrocarbon cracking, Zn-Cr oxide catalyst for the conversion of CO-H_2 mixtures to methanol, iron-molybdate for methanol oxidation. The supports are prepared by similar procedures (e.g. aluminas, silicas, silica aluminas).

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Table 1
Unit operations in catalyst preparation

1. Precipitation
2. Gelation
3. Hydrothermal transformation
4. Decantation, filtration, centrifugation
5. Washing
6. Drying
7. Calcination
8. Forming operation
9. Impregnation
10. Crushing and grinding
11. Mixing
12. Activation

Impregnated catalysts are usually obtained from preformed supports by impregnation with the active phase. Quite a number of hydrogenation catalysts are prepared in this way.

The last category of mixed-agglomerated catalysts comprises those catalysts obtained by mixing the active substances with a powdered support or a support precursor and then agglomerating the mixture. As far as the techniques are concerned, such catalysts can be considered bulk catalysts. But as the mixing operation often consists of impregnating a powder with a solution of the active substance precursors, the catalysts so obtained may be regarded as impregnated catalysts. Quite a number of catalysts for hydrotreating refinery processes can be classed in this hybrid category.

Based on the above considerations we will go on illustrating the main unit operations for bulk catalysts and supports preparation (Section 2). Then we will consider the preparation of supported catalysts by impregnation or by precipitation on a support (Section 3). The preparation of a zeolite catalyst will be given as an example in Section 4. Lastly we will carefully examine the problem of dispersion of the active components (Section 5).

2. Main unit operations for bulk catalyst and support preparation [2]

2.1. Precipitation [3,4]

The aim of this step is to precipitate a solid from a liquid solution. While each intermediate in the preparation chain can be considered the precursor of the following one, precipitation gives rise to the basic precursor, because it really creates the imprint or latent image of the final solid that subsequent operations will progressively reveal.

Precipitation occurs in three steps: supersaturation, nucleation and growth. Pertinent parameters producing supersaturation are shown in Fig. 1. Solubility curves are functions of temperatures and pH. In the supersaturation region the system is unstable and precipitation occurs with any small perturbation. The supersaturation region can be approached either by increasing the concentration through solvent evaporation (A to C), lowering the temperature (A to B) or increasing the pH (which moves the solubility curve to D and A into the supersaturation region). This last approach is quite usual in the preparation of hydroxides and sulfides. Particles within the supersaturation region develop in a two-stage process: nucleation and growth. Nucleation may proceed spontaneously (homogeneous nucleation) or be initiated with seed materials (heterogeneous nucleation). These are solid impurities such as the dust or the rough edges of the vessel surface. The rate of nucleation can be accelerated by deliberate addition of seed nuclei. The growth process depends on concentration, temperature, pH and ripening. The size of the precipitated crystal diminishes

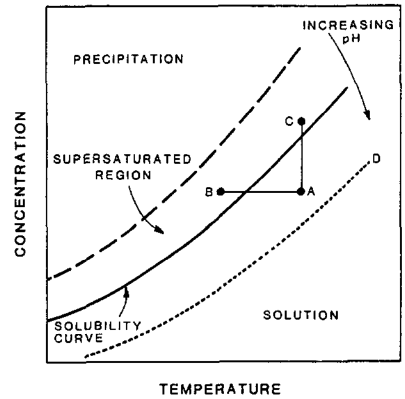


Fig. 1. Supersaturation dependence on concentration, T and pH (reprinted with kind permission from [4]. Copyright by Plenum Press).

as their equilibrium solubility diminishes (i.e. as supersaturation increases), as Ostwald ripening is slowed down by the reduced transfer rate between the suspended particles [1]. Most precipitates are crystalline precipitates. Depending on the precipitation conditions it is possible to obtain amorphous solids. If the supersaturation is very high, the aggregation rate can exceed the orientation rate and the solid obtained is amorphous. However, by ripening in the presence of the mother liquor, the amorphous solid can become crystalline. Precipitation can be performed starting from either 'true' solutions or colloidal solutions (sols). Fig. 2 shows the characteristics of such solutions [5]. Particles which show little or no attraction for water form hydrophobic colloids. These are easily flocculated and the resulting colloidal precipitates are easily filtered (e.g. arsenic trisulfide, silver chloride). Particles which show a strong affinity to water form hydrophilic colloids. These are very difficult to flocculate and the resulting jellylike mass is difficult to filter. Hydrophilic colloidal solutions can be prepared from many inorganic compounds, such as silicic acid and the hydrous oxides of aluminum and tin. We will consider such gels in Section 2.2.

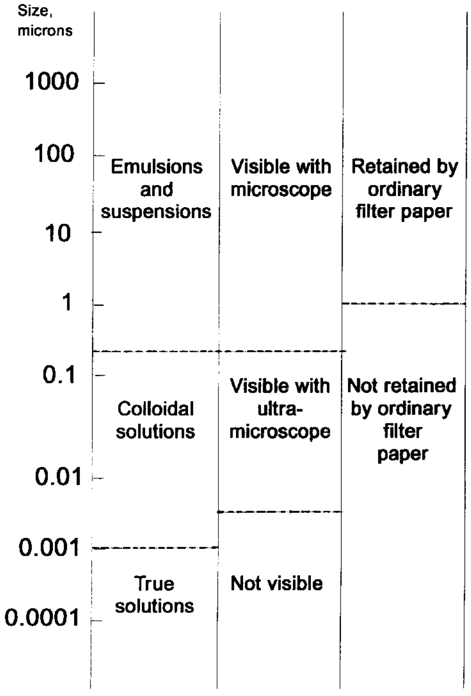


Fig. 2. Properties of colloidal particles [5].

Precipitation procedures can be used to prepare either single component catalysts and supports or mixed catalysts. The main purpose in the latter case is the intimate mixing of the catalyst components that can be achieved either by the formation of very small crystallites or by the formation of mixed crystallites containing the catalyst constituents. Hydroxides and carbonates are the preferred precipitated intermediates for the following reasons [6]:

(1) The solubility of these salts of transition metals are very low. Consequently, very high supersaturations can be reached, leading to very small precipitate particle sizes.

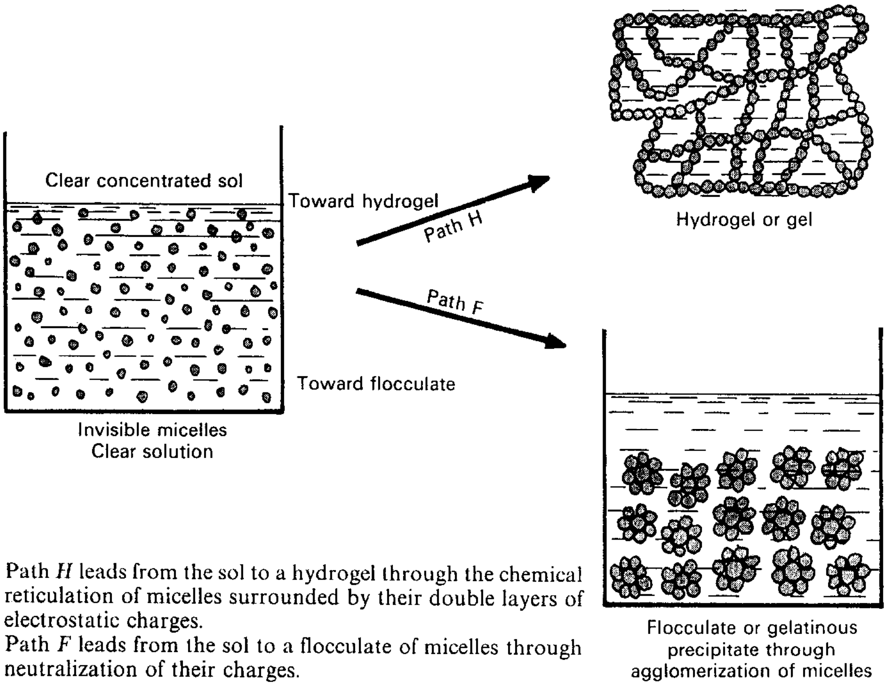
(2) Hydroxides and carbonates are easily decomposed by heat to oxides of high area without leaving potential catalyst poisons (as, for example, the sulfur left by sulfates calcination).

(3) Safety and environmental problems arising from the calcination of hydroxide and carbonates are minimal.

During coprecipitation care must be taken in order to avoid independent or consecutive precipitations. Besides, the pH should be adjusted and kept constant during the operation: this can be done by mixing the starting solution continuously, instead of adding one solution to the other [7].

2.2. *Gelation and flocculation [2,4]*

Hydrophilic colloidal solutions are formed of micelles that remain separated because of electrical charges on their surfaces and in the surrounding solution. These charges create repelling forces which prohibit coagulation of the micelles. Such micelles are produced via chemical reactions of polymerization and polycondensation. For instance, a silica sol can be obtained starting from sodium silicate and a mineral acid by polycondensation of the intermediate silicic acid.



Path *H* leads from the sol to a hydrogel through the chemical reticulation of micelles surrounded by their double layers of electrostatic charges.
Path *F* leads from the sol to a flocculate of micelles through neutralization of their charges.

Fig. 3. Formation of gels and flocculates (reprinted with kind permission from [2]. Copyright by Editions Technip).

The reticulation of these micelles gives rise to a hydrogel, a three-dimensional network that imprisons molecules of water. The mechanism of a hydrogel formation is reported in Fig. 3. The point at which this process, also called gelation, occurs depends on the concentration of micelles, the temperature, the ionic strength of the solution and especially on the pH. For silica sols the gelation time ranges from a few minutes to a hundred hours while the pH varies from 2 to 7 [8] (Fig. 4).

The density of the gel will increase with the concentration of the original salts in the solution and with the gelation rate. Cogel can be obtained by gelation of sols containing two or more species (SiO_2/Al_2O_3, SiO_2/Cr_2O_3).

The starting sol can also be obtained by hydrolysis of alkoxides such as tetraethyl orthosilicate. This is the first step in the well known sol–gel process largely used to produce homogeneous ceramics, glass and composites [9,10]. The sol–gel process can also be successfully applied for catalysts preparation [11].

Sol–gel methods have several promising advantages over precipitation. In general, sol–gel synthesis offers better control over surface area, pore volume and pore size distribution. Besides,

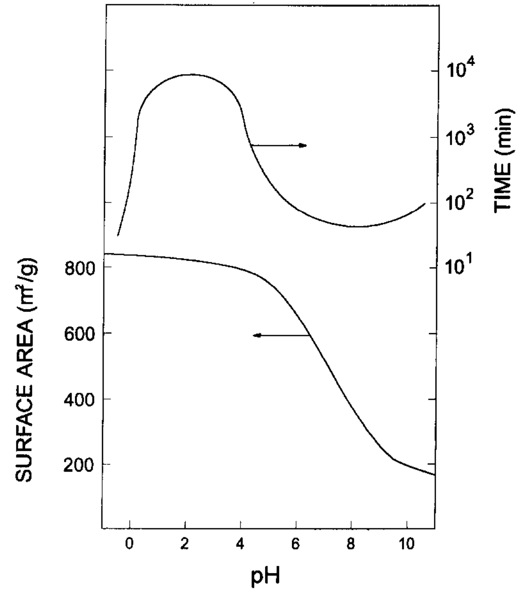


Fig. 4. Gelation of silica: influence of pH on gelation time (upper curve) and surface area (lower curve) [8].

the number of alkoxides commercially available allows the formulation of quite a number of cogel with high uniformity and stability.

The flocculation of a sol can be obtained through the neutralization of the micelle charges (Fig. 3). The micelles thus coagulate into flocculates that more or less precipitate well. Hydrophilic sols generally give jellylike flocculates that contain large amounts of water (e.g. the amorphous flocculate of $Al(OH)_3$). Such flocculates are denser than hydrogels, but in both cases the elementary solid particle has the dimensions of the original micelles. The surface area of the final solid depends on the original micelle size and also on the ripening and drying conditions.

2.3. *Hydrothermal transformations [2]*

For hydrothermal transformations we usually consider the modification of precipitates, gels or flocculates, induced by temperature, under aging or ripening in the presence of the mother liquor (usually water). These transformations are usually carried out at rather low temperatures (100–300°C). They involve textural or structural modifications of the solid that can be summarized as follow:

(1) small crystals → large crystals;

(2) small amorphous particles → large amorphous particles;

(3) amorphous solid → crystalline solid;

(4) crystal 1 → crystal 2;

(5) high porous gel → low porous gel (Aging or syneresis of a gel [10]).

All such transformations obey the laws of thermodynamics and thus proceed in a direction corresponding to a decrease in free energy of the system.

Increasing interest has been devoted in the last decades to the hydrothermal synthesis of zeolites and molecular sieves, which is a particular application of the hydrothermal transformations [12]. A detailed description of zeolite catalyst preparation will be given later (Section 4).

In most ripening treatments hydrothermal transformations usually occur within a liquid phase. However they can also be performed in an atmosphere of steam, such as the steam stabilization procedure of Y zeolites [13].

The variables of these types of operations for a given solid are: pH, temperature, pressure, time and concentration. When a hydrothermal transformation is distinct from other operations, it is carried out in specific reactors. In other instances the hydrothermal transformations are carried out during other unit operations such as precipitation, washing, drying, extrusion.

2.4. *Decantation, filtration, centrifugation and washing*

Decantation, filtration and centrifugation are well known unit operations, the aim of which is the separation of the solid phase from the mother liquor. Washing of the solids is then required to remove the mother liquor completely and to eliminate impurities.

The separation of the mother liquor is quite easy for crystalline precipitates, difficult for flocculates and of no use for hydrogels. The selection of the separation method will also depend on the particle size of the solids.

A satisfactory but time-consuming method is decantation [4]. Washing is carried out simultaneously with it. The slurry is added to a large volume of distilled water and the suspension is thoroughly mixed. Upon standing, particles settle down. When a definite interface is visible, water is removed by decantation and the process repeated till the desired purity is reached. When washing flocculates, problems may arise as the purified flocculate takes longer to settle with each washing, since removal of counter-ions reverts the flocculate to sol. This is the well known phenomenon called peptization. Care must be taken not to wash too much or allow settling times to become too long. When washing is completed the solid is filtered. If the particles are too small and the settling time too high, filtration or centrifugation must be used. Again care must be taken not to wash too much with water, otherwise the flocculates peptize and pass through the filter.

Washing can also be applied to exchange certain undesirable or useless ions for others that are easily decomposable by calcination. For this purpose a proper salt solution in water will be used instead of distilled water. High temperatures (e.g. 100°C) can increase the efficiency by increasing the exchange rate. For example the exchange of Na^+ for NH_4^+ is used to obtain the ammonium form of a zeolite, which is transformed into the acidic form by calcination [14].

2.5. Drying [4]

Drying is described as 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 for hydrogels that can contain up to 90% of water. Therefore we will discuss only the drying of such gels.

The removal of water can result in a certain collapse of the structure. Care must be taken to properly control the drying operations if high porosity is desired.

Initially drying occurs through evaporation of moisture from the outside surface of hydrogel. The water loss rate is constant 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 about 50%. Then the gel mass begins to shrink. The material so obtained is called xerogel.

The subsequent moisture loss occurs with a declining rate, in which evaporation is controlled by capillary forces. The saturation point decreases as pores become smaller and evaporation slows until water is forced into larger pores by concentration gradients. If evaporation occurs but 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. The pore volume loss on drying of a silica hydrogel is reported in Fig. 5 [4]. High temperature gradients should be avoided in order to reduce such effects. The effect of temperature is shown in Fig. 6. Gel breakage is reduced by lowering the drying temperature, increasing the relative humidity of the drying medium or reducing airflow through the gel bed [15]. Vacuum drying at lower temperatures is an advisable laboratory procedure.

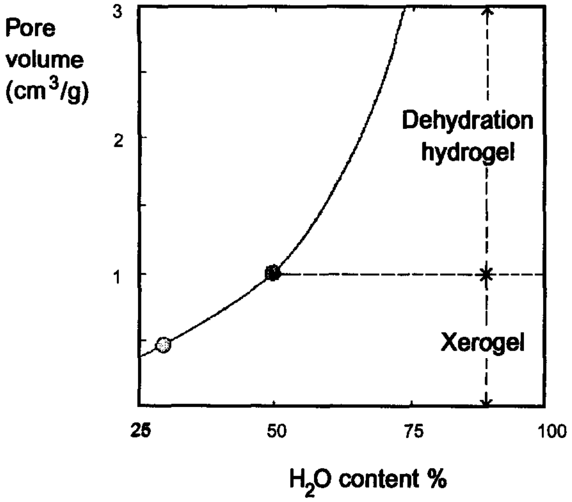


Fig. 5. Pore volume reduction on drying a silica hydrogel [4].

Dried xerogels contain 25–30% of water, encapsulated in fine pores or chemically bound to the oxide. In this moist state it is sometimes easier to form the material into pellets or extrudates. This is sometimes done for convenience,

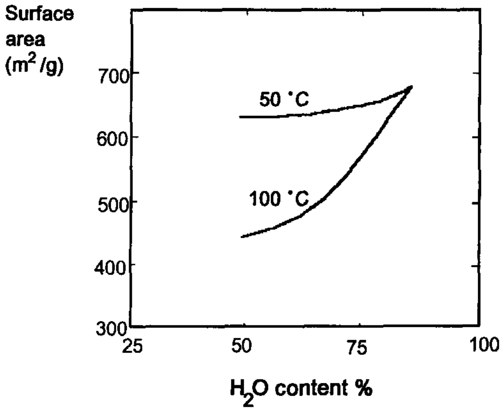


Fig. 6. Effect of drying temperature on the surface area of a silica hydrogel [4].

provided subsequent calcination does not weaken or damage the particles.

Large capillary stresses can be avoided by operating at temperatures higher than the critical temperature of water or by vaporizing the water under vacuum at temperatures ranging from −50 to −5°C [2]. The solid structure undergoes only a small modification by retaining the textural properties of the wet gel and leading to a highly porous dry solid called aerogel [16].

2.6. Calcination

Calcination is a further heat-treatment beyond drying. As with drying, this unit operation can be located before or after the forming operation, depending on the case. We will refer in the following to calcination in air, typically at temperatures higher than those used in the catalytic reaction and catalyst regeneration. Other thermal treatments, such as reductions or sulfidations, are performed in special atmospheres, so they will be designated as activation operations. The latter are usually performed in the industrial reactor at the start-up of the unit. Therefore they are not considered to be preparation procedures. Several processes occur during calcination: loss of the chemically bonded water or CO_2, modification of the texture through sintering (small crystals or particles which turn into bigger ones), modification of the structure, active phase generation and stabilization of mechanical properties. Alumina is a good example with which to demonstrate all these features. Fig. 7 outlines the principal decomposition sequences that occur upon heating the aluminum hydroxide [4]. Upon calcination of bohemite above 300°C, a series of phase changes occur, simultaneously with loss of hydroxyl groups and hence of water. These result in the formation of a series of oxides (η-, γ- and δ-phases), known as pseudo γ-alumina, good for binder and catalysts support, and therefore useful ingredients in catalyst preparation [17]. Above 1000°C monoclinic θ-Al_2O_3 forms, transforming into hexagonal α-Al_2O_3 at 1200°C. These are anhydrous, low surface area oxides and are not suitable for porous supports. They are used in applications where mechanical strength is required. Changing the calcination temperature, even when phase transitions are avoided, can affect the pore size distribution. In Fig. 8 is reported the effect of the calcination temperature on a γ-alumina [4]: increasing the temperature results in a collapse of micropores and in the increase of the mean pore size.

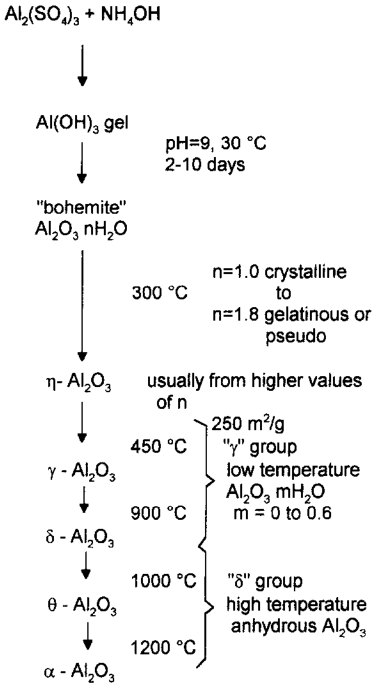


Fig. 7. Alumina modification upon calcination [4].

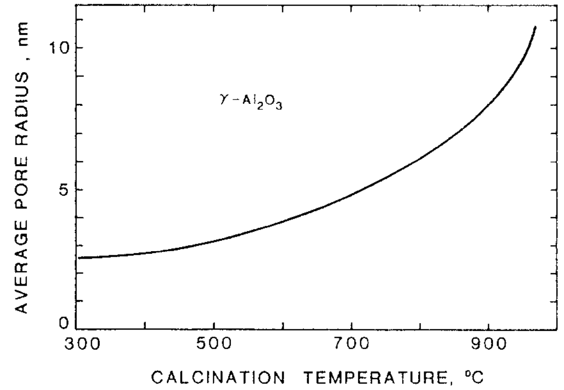


Fig. 8. Effect of calcination temperature on the pore size of γ-Al_2O_3 (reprinted with kind permission from [4]. Copyright by Plenum Press).

By calcining a xerogel various types of sintering can result with two extremes: (1) sintering at constant pore radius and (2) sintering at constant pore volume [2].

The first is the case of a xerogel with covalent bonds (silica and silica-alumina), calcined in dry air. The textural modification results in a contraction of the untouched xerogel around pinpoints of crystallization. The overall pore volume reduces.

The second case is typified by ferric hydroxide, a xerogel with ionic bonds, which retains its pore volume, even in dry air, by calcination and sintering. The particles get bigger and the pore size increases.

Between the two extremes the intermediate cases are observed. Thus calcining a xerogel with covalent bonds in the presence of steam results in a sintering at constant pore volume. The addition of a specific agent can affect the sintering. For instance the addition of sodium to silica lowers the sintering temperature. A substance which inhibits the sintering is called textural promoter [17].

In conclusion, the calcination operating variables for a given gel are time and temperature and the presence of steam.

2.7. Forming operations

Forming operations are applied to obtain suitably sized particles of catalyst to be used in the reactor. Therefore, forming and shaping of supports and catalysts is an important step in the preparation procedure of a catalyst. A catalyst particle shape and dimension should promote catalytic activity, strengthen the particle resistance to crushing and abrasion, minimize bed pressure drop, lessen fabrication cost and distribute dust build-up uniformly. Unfortunately, these objectives are not easily achieved. Indeed, several are mutually exclusive. For instance, a smaller particle size increases activity but also increases bed pressure drop. The best operational catalyst, therefore, has the shape and size that, in the end, represent the optimum economic trade-off [18]. The selection of the shape and size is driven by the type of reactor. Table 2 gives a rough survey of the different shapes and the reactors in which they are used [19]. For a given reactor the shape and the size of the catalytic particles will depend on the hydrodynamic and on heat and mass transfer limitations. Here we will describe the different techniques for shaping the catalysts into the shape mentioned in Table 2.

Table 2
Different types of catalyst shapes [19]

Shape	Size	Type of reactor
Extrudate	$d = 1–50$ mm $l = 3–30$ mm	Fixed bed reactor
Pellet	$d = 3–15$ mm $h = 3–15$ mm	Fixed bed reactor
Granule, Bead	$d = 1–20$ mm $d = 1–5$ mm	Fixed bed reactor
Sphere	$d = 1–10$ mm	Fixed bed reactor Moving bed reactor
Microspheroidal	$d = 20–100$ μm	Fluid bed reactor Slurry reactor

Two extreme types of shaping can be distinguished [2], depending on whether the desired products are powder microgranules or grains of the size order of one to several millimeters.

2.7.1. Forming microgranules (20–100 μm)

Crushing and grinding are of no use to produce microgranules for such a purpose. Actually the powder so obtained has a broad particle size distribution, with a lower limit of few microns. Such a powder is not usable in fluidized beds because of its poor mechanical resistance. Spray drying is a suitable technique to produce microspherical materials. In a spray dryer a hydrogel or a sol is sprayed through nozzles into a heated zone. Depending on the temperature, either drying or both drying and calcination occur as the drops fall. Examples of catalyst produced by this procedure are: catalytic cracking catalysts (silica-alumina doped with X or Y type zeolites) [22]; titanium silicalite catalyst [20]; silica gel [8].

The process itself is more art than science

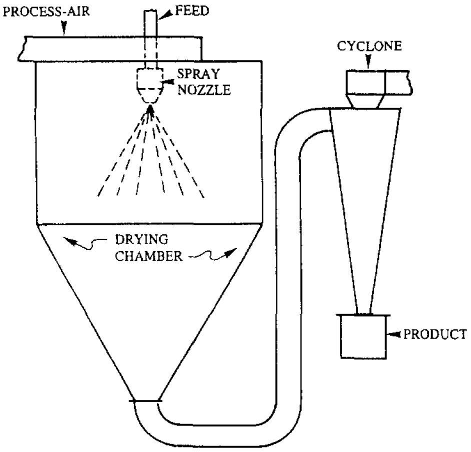


Fig. 9. Spray dryer (reprinted with kind permission from [19]. Copyright by Elsevier Science B.V.).

[19]. There is hardly any information in the open scientific literature [21]. Important process parameters are the viscosity of the liquid, the solid content of the suspension, the film-forming characteristics, the type of atomizer, the temperature, the gas velocity. In Fig. 9 is reported the scheme of a spray dryer. Fig. 10 shows two different kinds of particles obtained by different feeds.

2.7.2. *Forming grains (> 1 mm)*

The raw materials comprise a calibrated powder or paste with suitable rheological properties. Table 3 summarizes the methods used for making grains according to the nature of the original charge.

2.7.2.1. Extrusion and wet pressing. Extrusion is the most commonly applied shaping technique for catalysts and catalyst supports. A wet paste is forced through a die. As the ribbon of the extrudate paste emerges from the die it is cut to the desired length by a proper device. Usually catalyst mixes of powdered oxides made by precipitation do not by themselves have the necessary mouldability and plasticity even when the optimum water content is added. They behave rather like sand.

Besides, quite a number of such materials

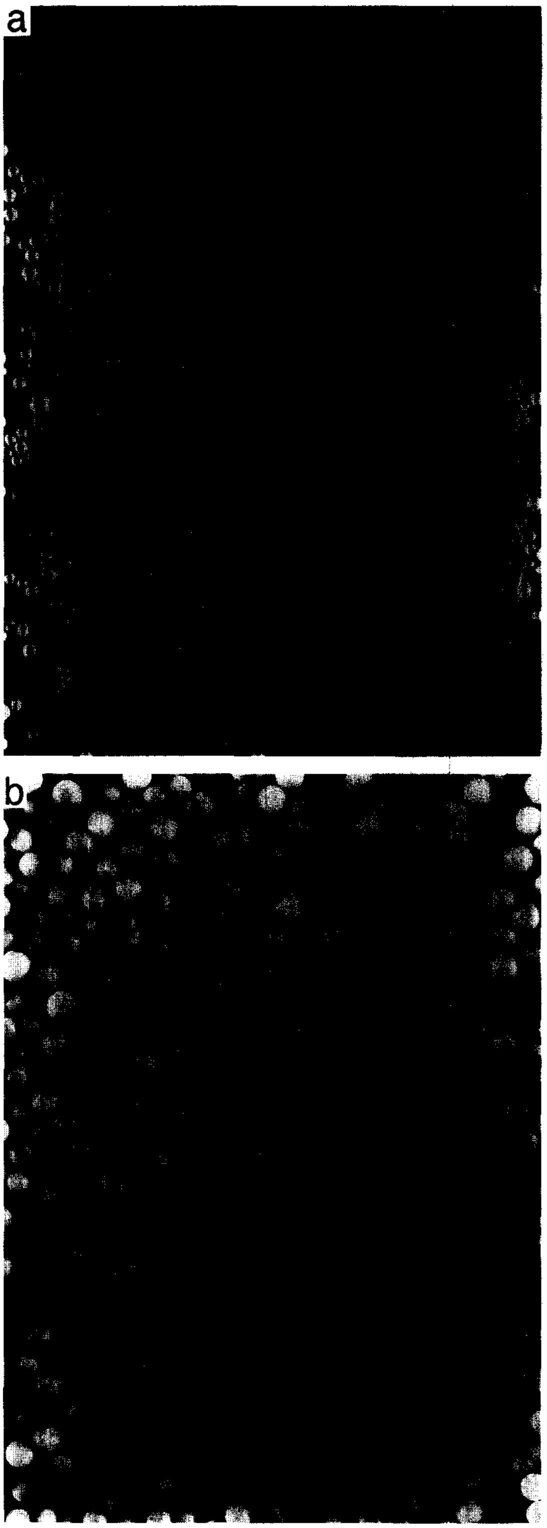


Fig. 10. Microgranules obtained by spray drying: (a) titania; (b) silica-alumina.

Table 3
Influence of the starting material on the choice of grain-forming process [2]

Starting material	Process
Monolithic blocks	Crushing and grinding
Powders	Dry tabletting
	Granulation
	Extrusion
Pastes, hydrogels	Extrusion, wet pressing
Sols	Drop coagulation

need a binder to produce extrudates with good mechanical behavior.

So in the formulation of the paste different additives can be used:

compounds for improving the rheological behavior of the paste (clays or starch);

binders (aluminas, clays);

peptizing agents to deagglomerate the particles (acetic acid, nitric acid);

combustible materials to increase the macroporosity (the so called pore formers like carbon black, starch).

Extruding equipment can be classed in one of two categories: press extruders (for wet pressing) and screw extruders. The operating variables include: mixing time, additives content, water content, paste aging, extrusion temperature. The quality of the extrudates will also depend on the drying and calcining procedure.

Special shapes such as trilobates, rings, hollow cylinders can be obtained by using proper dies. Monolith or honeycomb supports are also manufactured by extrusion of a thick inorganic dough through a special die. Such unusual support form is used in automobile catalytic converters, where a very low pressure drop is required to minimize power loss from the engine [17].

2.7.2.2. *Dry tabletting*. In this shaping process a dry powder is pressed between two punches in a tabletting press.

The production of strong particles by tabletting requires that the particles of the tablet feed be subjected to a reasonably uniform triaxial pressure and that under this pressure they are crushed together to form a dense bed which then welds at points of contact. At the tabletting stresses capable of being generated by normal 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 Moh's scale of hardness. This is shown in Fig. 11 [7]. Additives such as lubricants (mineral oil, talc, graphite, various stearates) and binders (bohemite, clays) are added to give the powders proper qualities. For example, when tabletting untablettable material such as Cu_2O, Al_2O_3 (see Fig. 11), a sufficient quantity of hydroxide or carbonate precursor is left in the tabletting feed (e.g. $CuCO_3$, $Al(OH)_3$) to act as binder [7]. The tabletting pressure heavily affects the porosity of the tablet. This is shown in Fig. 12 for the tabletting of bohemite [23].

Compared to other shaping methods tabletting is quite an expensive method.

Tabletting is widely used as preliminary forming method in order to prepare samples for catalyst testing in fixed bed microreactors, starting from powders. Depending on the reactor diameter the pellets are then crushed and sieved

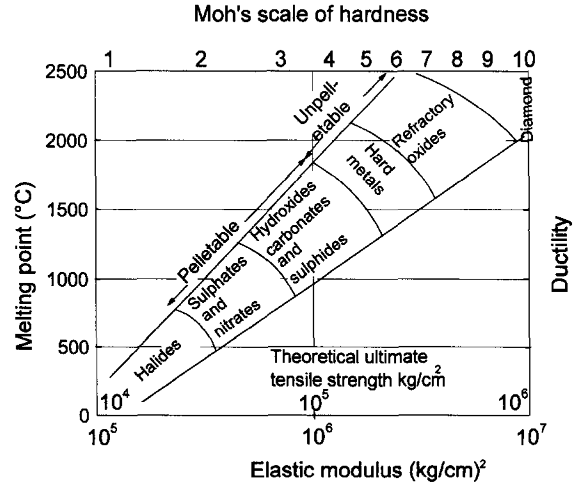


Fig. 11. The relation among pelletability, crystal strength and melting point [7].

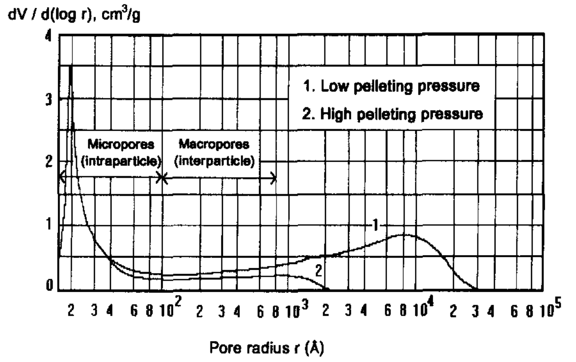


Fig. 12. Influence of pelleting pressure on bohemite pore size distribution [23].

to a suitable particle size (reactor to particle diameter ratios of 5–10) [4].

2.7.2.3. Granulation. Granules are particles with more or less spherical shape. The diameter of these particles ranges between 2 to 30 mm. The principle of the shaping method is best described by the snowball effect [19]. A round dish (see Fig. 13) rotating on an inclined axis is used. Small particles are fed into the dish. At the same time a cohesive slurry is sprayed onto the particles. The particle surface becomes wet and granules begin to grow. The small particles rotating develop layer by layer into larger, more or less spherical particles. After drying, the green spheres are calcined to obtain higher mechanical strength. Sometimes some binder and

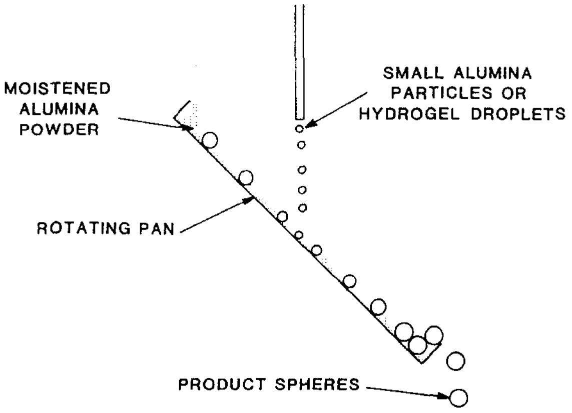


Fig. 13. Production of spheres by rotating dish granulator (reprinted with kind permission from [4]. Copyright by Plenum Press).

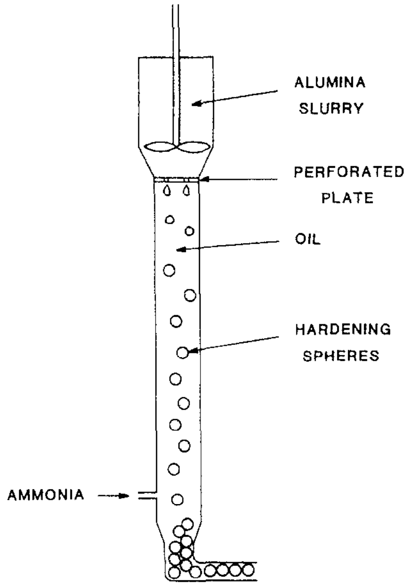


Fig. 14. Production of spheres by drop coagulation (reprinted with kind permission from [4]. Copyright by Plenum Press).

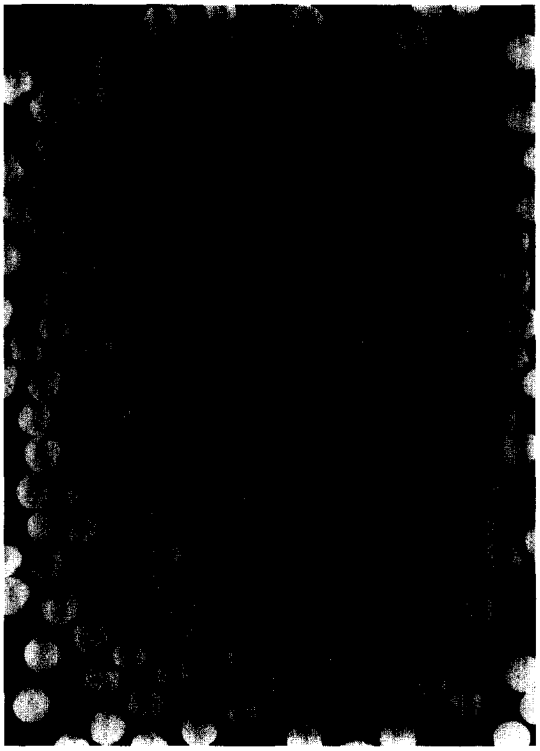


Fig. 15. Alumina spheres obtained by drop-coagulation.

cement are used to make the layers adhere better.

2.7.2.4. Drop coagulation (sol–gel method). Drop coagulation results from sols suspended in an immiscible liquid, by simultaneous gelation, ripening and forming. Fig. 14 illustrates the principle of the method. In the form of droplets the aqueous sol is forced, through a sparger in a water-immiscible solvent, the temperature of which is raised to around 100°C. The surface tension created on the droplets permits the formation of gel spheres that are than ripened and dried. The gelation can also be induced by increasing the pH [4]. During drying a contraction of the bead without deterioration is observed as long as the diameter is not too large. Accordingly, this method is suitable for producing beads such as alumina beads used as support (Fig. 15).

3. Supported catalysts

Supported catalysts are often applied because they combine a relatively high dispersion (amount of active surface) with a high degree of thermostability of the catalytic component.

The preparation of supported catalysts aligns all the unit operations toward dispersing an active agent on a support, that may be inert or catalytically active. The wetting of the support with a solution or a slurry of the active phase precursors is the operation that characterizes such a preparation. The other operations (drying, washing, calcination, forming) are ruled by the same laws, depend on the same parameters and use the same equipment described in Section 2.

The function of a support is, quite simply, to enable the formation of a large particle or tablet of catalyst composed of very small readily sinterable crystals of catalyst which are prevented from coalescing by being separated from each other by the support component. The support component clearly has to be much more resistant to sintering than the catalytic species. Two methods of utilizing support are common [7]. Firstly, a support may be used as a form of refractory surface on which the catalyst crystals are dispersed; rather like putting small drops of mercury on a table top. Secondly, the support may be used in the form of more finely divided refractory crystals than the catalytic species, positioned between particles of such species so that they are kept out of contact – rather like dust which can be used to stop a heap of mercury drops from coalescing. With the first method, the volume of support is considerably greater than the volume of catalytic species, consequently this method is normally employed with precious metal. The preferred preparation procedure for such catalysts is impregnation on a preformed support.

Preparation procedures for the second type of catalysts usually start from powders of support or support precursors (e.g. precipitation of active species on powder support). Then a forming operation will follow.

A thorough description of the techniques for the dispersion of the active components will be given in Section 5. In this section we will consider the support selection (Section 3.2) and the most common preparation methods: precipitation (Section 3.2) and impregnation (Section 3.3).

3.1. Support selection

The selection of a support is based on its having certain desirable characteristics. Principally they are [17]:

1. Inertness.

2. Desirable mechanical properties, including attrition resistance, hardness and compressive strength.

3. Stability under reaction and regeneration conditions.

4. Surface area. High surface area is usually, but not always, desirable.

5. Porosity, including average pore size and pore size distribution. High area implies fine

pores, but relatively small pores (for example < 5 nm) could become plugged during impregnation, especially if high loading is sought.

6. Low cost.

Of a wide variety of possible materials, only three of them possess a good combination of the characteristics mentioned: alumina, silica and activated carbon. Alumina is the most widely used industrially.

Table 4 reports the main characteristics of some typical supports [24]. Materials with low surface area are generally useful in supporting very active catalytic components in reaction where further side reactions may affect activity and selectivity. Examples of catalysts prepared with low surface area supports are: Fischer–Tropsch cobalt catalyst on diatomaceous earth and ethylene oxide silver catalyst on pumice [24]. Supports with high surface area are widely used in precious metal catalyst preparation.

3.2. Precipitation [4]

In precipitation, the objective is to achieve a reaction of the type:

Metal Salt Solution	+	Support	→
oxalate		powder	NaOH
nitrate		particle	KOH
sulfate			NH_4OH
			$NaHCO_3$

Metal hydroxide or carbonate on support

The choice of the salt or alkali depends on factors similar to those considered in Section 2.1. Powders or particles are slurred with an amount of salt sufficient to give the required loading.

Enough alkali solution is added to cause precipitation, the powder is then treated with the same operations already discussed for bulk catalyst preparation. When preformed support is used forming operations are avoided.

Two process are involved in the deposition: (1) precipitation of solution in bulk and pore fluid; (2) interaction with the support surface. Best results occur when the OH groups of the support interact with the metal. For example, silanols group of silica interact with $Ni(NO_3)_2$, resulting in a surface hydrosilicate formation, rather than hydroxide deposition [25].

Rapid nucleation and growth in the bulk solution must be avoided, since it produces a deposition only outside the support porosity. An effective method to obtain a uniform precipitation is to use urea rather than conventional alkalis. Urea dissolves in water but decomposes very slowly at 90°C, giving a uniform concentration of OH^- in the bulk and in the pores. So precipitation takes place homogeneously over the support surface [25].

The precipitation is the preferred deposition route for loading higher than 10–20%. Below this value, impregnation is usually practiced.

3.3. Impregnation

The impregnation method involves three steps: (1) contacting the support with the impregnating solution for a certain period of time, (2) drying the support to remove the imbibed liquid and (3) activating the catalyst by calcination, reduction or other appropriate treatment. Two methods of contacting may be distinguished, depending on the total amount of solution.

(1) With excess of solution. The support is placed on a screen and dipped into an excess quantity of solution for the time necessary for total impregnation. The solid is then drained and dried. This operation can be done continuously as shown in Fig. 16a. In such an operation the composition of the batch solution will change and the release of debris can form a mud which makes it difficult to completely utilize the solution [17].

(2) With repeated application of solution. A more precise control is achieved by this technique, termed dry impregnation or impregnation to incipient wetness. The support is contacted with a solution of appropriate concentration, corresponding in quantity to the total known pore volume or slightly less [17]. This operation

Table 4
Typical catalyst support [24]

Support	Specific surface area (m^2/g)	Pore volume (ml/g)
Low area:		
Alundum, Norton	0–1	0.33–0.45
Corundum, Alcoa T-61	0.07–0.34	0.08
Silicon carbide, carborundum	< 1	0.40
Pumice, Italian	0.04	
Diatomaceous earth	2–30	0.5–6.1
Asbestos	1–16	
Firebrick	< 1	
High area:		
Alumina:		
Alcoa F-10	100	0.3
Alcoa XF-21	200	0.2
Silica-alumina:		
Alcoa H-41	350	0.5
Cracking catalysts	400–600	0.6–0.9
Bauxite	150	0.25
Clays, bentonite	150–280	0.3–0.5
Magnesia	30–140	0.3
Silica gel	400–800	0.4–4.0
Activated carbon	90–1100	0.3–2.0

can be performed continuously as shown in Fig. 16b. The catalyst is kept in motion in a rotating cylinder or drum, and is sprinkled as required with a solution of salt by sprayers. The disadvantage is the poorer distribution of the precursors [2].

For both techniques the main operating variable is the temperature which affects both the precursor solubility and the solution viscosity and, as a consequence, the wetting time.

In Fig. 17 are shown four limiting types of impregnation profiles. A proper control of the operating conditions during impregnation and drying determines the impregnation profile of the final catalyst [26].

4. Zeolite catalyst preparation: an example

Zeolite are crystalline aluminosilicates with a framework structure enclosing channels in which cations and water molecules are located. The general empirical formula of zeolites is: $(M^{n+})_{x/n}(AlO_2)_x(SiO_2)_y mH_2O$, where M is a cation, m is the number of moles of water of crystallization and $(x+y)$ gives the number of AlO_4 and SiO_4 tetrahedra in the unit cell. In the zeolites that are catalytically active for hydrocarbon transformation, M^{n+} is typically H^+; the catalytic activity is associated with the Bronsted and Lewis acid sites within the crystalline structure [27].

Zeolites are usually crystallized from alkaline aqueous gels at temperatures roughly between 70 and 300°C. The composition of the reaction mixture is suitably defined by a set of molar ratios SiO_2/Al_2O_3 H_2O/SiO_2 OH^-/SiO_2 M^+/SiO_2 where M^+ represents an alkali, alkaline earth or ammonium ions. Most of the early work in the synthesis of zeolites involves crystallization of the alumosilicate gel from a solution containing alkali hydroxide as the base. In Table 5 the most commonly used source of cations, aluminum and silicon are reported. Barrer [12] discovered that the presence of organic cations along with the alkali led to more open crystal structures. The results of research efforts in the use of organic cations during zeolite synthesis have led to the discovery of many new zeolite materials [28]. Among them, ZSM-5 is the most interesting for catalytic application [29]. So the preparation of a ZSM-5 zeolite catalyst will be discussed as an example.

4.1. Preparation of a ZSM-5 zeolite catalyst

The preparation of a zeolite catalyst consists of the following main steps:

1. Hydrothermal synthesis of zeolite;
2. Ionic exchange to obtain the acidic form;
3. Binding and shaping.

A schematic diagram of the first and the second steps for ZSM-5 preparation is reported in Fig. 18, according to Jacobs [30].

(1) Hydrothermal synthesis. For the synthesis of ZSM-5 Aerosil (Grace Davison) as silica source is added to an aqueous solutions of tetrapropyl ammonium hydroxide (TPAOH). Sodium aluminate is dissolved in a concentrated NaOH solution and added to the first solution under vigorous stirring. The gel formed has the following molar composition: $(TPA_2O)_{24}(Na_2O)_{0.3}(Al_2O_3)(SiO_2)_{60}(H_2O)_{1550}$. The gel is transferred to an autoclave and

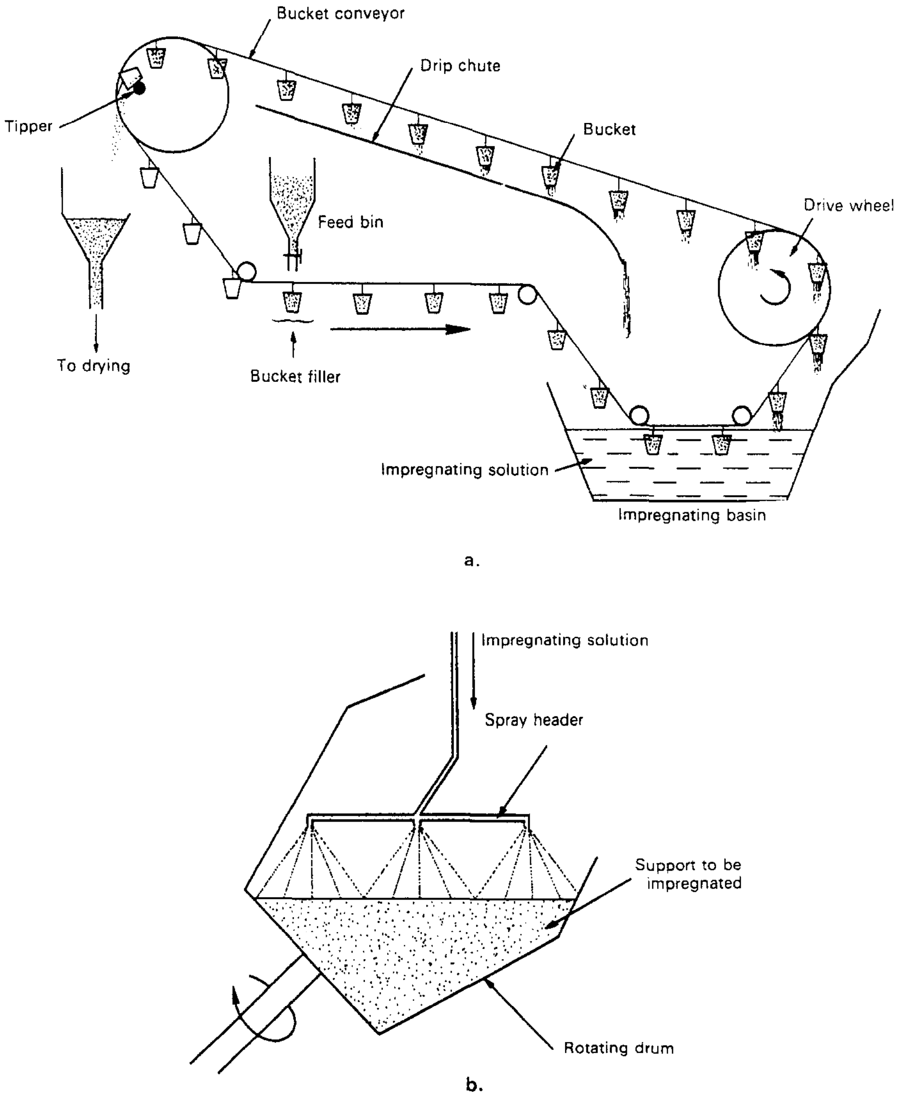


Fig. 16. Support impregnation processes: (a) with excess of solution; (b) impregnation to incipient wetness (reprinted with kind permission from [2]. Copyright by Editions Technip).

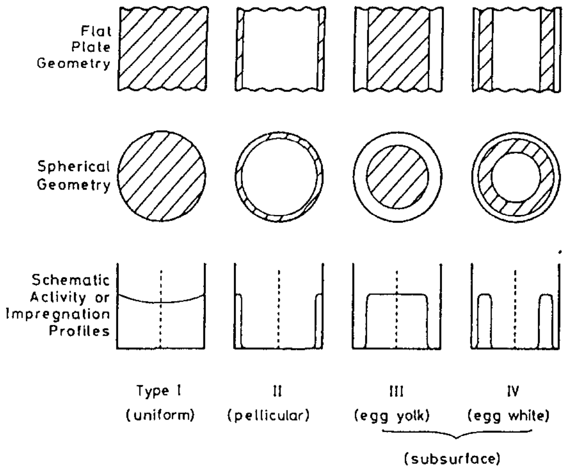


Fig. 17. Four limiting types of impregnation or activity profiles. Hatched areas in the cross sections of slabs and pellets (top and middle rows) indicate the regions where active components are deposited. The bottom row shows schematic examples of impregnation or activity profiles (reprinted with kind permission from [26]. Copyright by Marcel Dekker, Inc.).

stirred at 150°C for 3 days. Under ripening crystallization occurs. The solid so obtained is filtered, washed five times with distilled water and dried.

(2) Ionic exchange. The solid obtained contains both Na^+ and TPAOH. The latter must be removed from the zeolite framework to allow access to the intercrystalline pore channel system. This is usually performed by thermal de-

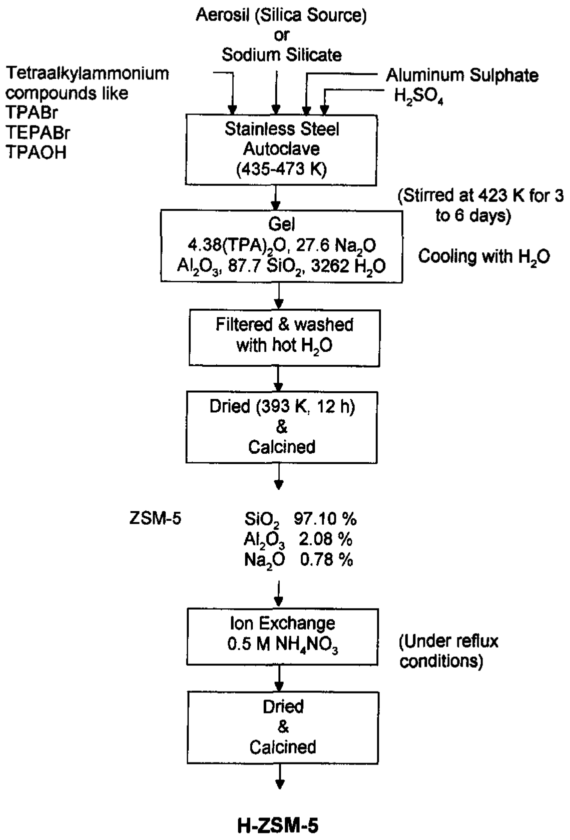


Fig. 18. Schematic diagram of ZSM-5 preparation [30].

composition and burning. So the solid is calcined under a flow of dry nitrogen at 300°C, the heating rate being 1°C/min. Calcination up to

Table 5
Most common used source of cations, aluminum on silicon in zeolite synthesis [14]

Charge compensating cations	Aluminum	Silicon
Alkali metal hydroxides	Metal aluminates	Silicates and silicate hydrates
Alkaline earth hydroxides and oxides	$Al(OH)_3$, Al_2O_3, AlO-OH Al alkoxides	Water glass
Other oxides and hydroxides	Al salts	Silica sols
	Glasses	Silica gels
Salts (fluorides, halides, carbonates, phosphates, sulfates, etc.)	Sediments	Silica and other synthetic glasses
	Minerals, especially clay minerals, fel-sphathoids and other zeolites	Silicon esters
		Tuffs and volcanic glass minerals, including clay minerals, felspathoids, feldspars, and other zeolites
Silicates and aluminates		Basalts and mineral mixtures
Mixtures of two or more of the above		Sediments
		Combinations of two or more of the above

550°C is continued for 3 h in air flow. Decomposition of the organic cation leads to the formation of protonic sites, but the complete transformation into the acidic form requires the elimination of Na^+.

This is obtained by exchange under reflux condition with 0.5 M solution of NH_4NO_3 at a liquid to solid ratio of 50. This is repeated several times, depending on the desired efficiency. The solid is then dried and calcined at 550°C under air flow.

(3) Binding and forming. Extrusion is a widely applied method of shaping a zeolite into a pellet. For this a purpose a binder must be used. In fact by extruding the zeolite alone poor mechanical strengths are obtained. The binder can be selected among aluminas and silica-aluminas. In this case a pseudo-bohemite (Laroche V-450) is added with the zeolite powder in a weight ratio of 1. A paste is obtained by mixing the powder with an aqueous solution containing a plasticizer (1% Methocel, Fluka) and a peptizer (acetic acid, 2% of pseudo-bohemite). The mixing is performed in a Z-blade mixer till a homogeneous paste is obtained (about 2 h). The paste is then aged at room temperature for 2 h and extruded. The extrudate is then aged (overnight, at room temperature), dried (at 100°C under vacuum) and calcined (at 550°C in air flow for 10 h). The extrudate (cylinders of 2 × 3 mm) so obtained contains ZSM-5 (60.5%) and Al_2O_3 (39.5%).

5. Techniques used to disperse the active species

5.1. Introduction

One of the most peculiar and relevant requirements for a solid catalyst to be of practical use is an appropriate dispersion of the active species. A high dispersion is usually desired because it corresponds to a greater utilization of the active species [1], since the catalytic phenomena occur at the surface of the solid. Thus porous solids with a high internal surface area are often necessary in order to reach reasonable values of activity. The porous texture is the result of the preparation unit operations for the unsupported catalysts or it will be supplied by the support itself in the case of supported catalysts.

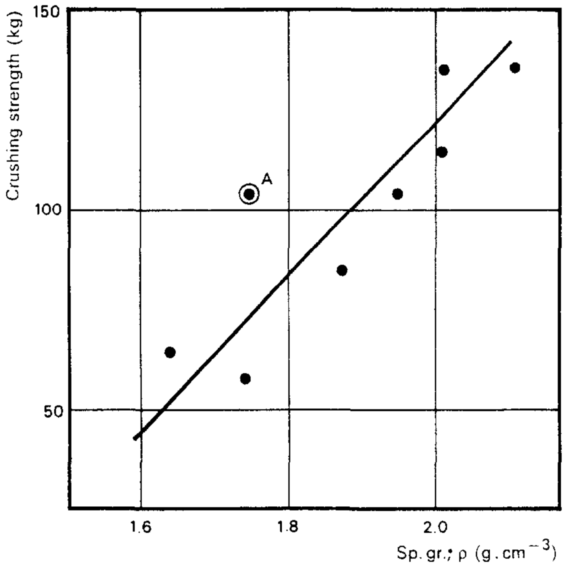


Fig. 19. Relation between density and grain-to-crushing strength of a iron-molybdate methanol-oxidation catalyst pellet. Point A corresponds to a powder of different texture before compacting. By increasing the pore volume the pellet density decreases according to $1/\rho = (1/\rho_s) + V_p$ where ρ_s is the structural (real) density (reprinted with kind permission from [2]. Copyright by Editions Technip).

Higher surface areas may be obtained to some extent, ceteris paribus, by increasing the pore volume. However, the mechanical properties of the catalyst pellet are, in general, negatively affected by an increase of the pore volume as shown by Fig. 19 [2].

To a greater extent the surface area may be increased by decreasing the mean pore width value of the catalyst. Indeed it may easily be shown that the surface area S is related to the pore volume V_p and pore radius r_p in a model

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[1] Dispersion is, by definition, the ratio of the active species present at the surface and those present in the bulk of the solid.

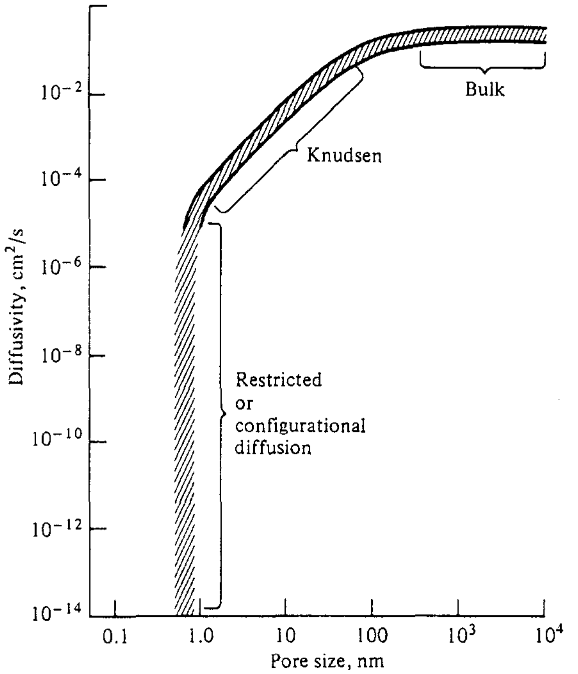

Fig. 20. Effect of pore size on diffusivity (reprinted with kind permission from P.B. Weisz, Chemtech, 3 (1973) 498. Copyright by the American Chemical Society).

with cylindrical monomodal pores by the expression:

$$S = 2V_p/r_p$$

Therefore the smaller the pore width the greater the surface area.

However if the pore dimension becomes too small, the internal diffusion of the reagents and products from and to the external surface is hampered as shown by Fig. 20 [31].

This is one of the reasons for which zeolites are used in association with binders which are provided with relatively wider pore structures. In the presence of diffusion limitations due to small pore values, the kinetic regime followed by the catalytic reaction will pass from the chemical region to the internal-diffusion-limited region. In this case the activity of the catalyst will be affected [32] and where more than a single reaction takes place a change of the selectivity to the various products may also be affected [33]. This is the reason why in many selective oxidations a moderate internal surface is more suitable. In an extreme case the oxidation of NH_3 to NO is performed on a Pt/Rh gauze (which has no porosity) and not on precious metals supported on a porous carrier: the reaction is carried out at ca. 850°C, and is controlled by the external diffusion of NH_3 onto the surface of the gauze. If the same reaction were performed on a porous catalyst, the internal diffusion would increase the selectivity to the unwanted product N_2, instead of NO.

Therefore, the preparation of a suitable catalyst will take into consideration the different aspects involved and often the most satisfactory catalyst will be a compromise between different requirements.

In any case, the preparation and production of a catalyst must be split into several well defined unit operations, which must be reproducible and uniform also during the scaling-up.

5.2. Preparation of single phases containing all the active elements

Solid catalysts are often multicomponent, i.e. their formulation contains different elements, all of which have some specific role. The association of these elements develops the greatest synergism if they are all present at the scale where the catalytic phenomenon takes place, i.e. the atomic scale.

Thus a catalyst must have an appropriate surface area (dispersion) but also a good interspersion of the various constituent elements.

The preparation of a catalyst must reach these two general goals.

As already reported in Section 2 the most used and preferred sequence for a catalyst preparation starts with a precipitation. If the nature of the active phase, including its chemical composition, has already been established, it is necessary to find out, by theoretical considerations and experimental tests, the values of the most convenient preparation parameters such as pH, temperature, reagents concentration, order of mixing, aging of the slurry, etc. For example Trifirò et al. [34] make the point of the influence of such parameters in the preparation of molybdates and tungstates. Highly concentrated solutions are generally utilized to favor nucleation vs. crystal growth rate so as to obtain a precipitate made of many small crystallites which lead, after calcination, to a high surface area. These conditions, although essential, make it necessary to manipulate slurries containing a solid of small particle size and may create some complications in the unit operations that follow particularly where decantation and filtration are concerned.

Furthermore, to obtain a good interspersion of the different elements inside the precipitate, independent or consecutive precipitation must be avoided. For example, in coprecipitation of Cu-Zn-Al hydroxycarbonates, which are the precursors of the low-temperature methanol synthesis catalysts, if the sodium carbonate solution is added to the nitrate solution, Al precipitates first at a pH of about 2.5, then Cu at about 3.0, then Zn at 4.5, as shown in Fig. 21.

To avoid this happening it is necessary to operate at constant pH during precipitation or to reverse the mixing order, i.e. to add the nitrate solution containing Cu Zn Al ions into the sodium carbonate solution.

If the desired phase cannot be formed by coprecipitation, other routes may be tested. In particular increasing attention has recently been given to the sol gel process, which also offers some advantage (see Section 2.2) and is also now better understood in its theoretical bases [35].

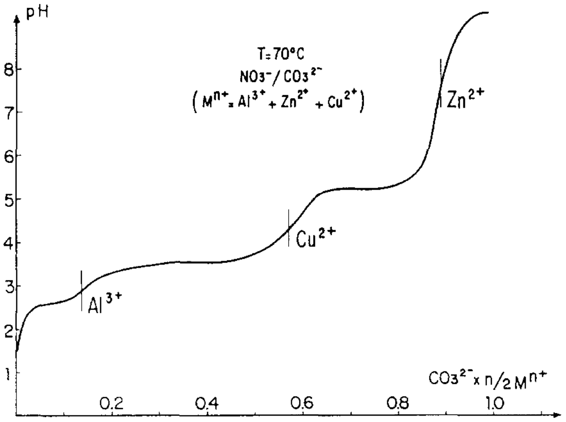

Fig. 21. Neutralization of Cu^{2+} Zn^{2+} Al^{3+} nitrate solution (0.35 M) with a Na_2CO_3 solution (0.4 M) pH vs. Na_2CO_3 equivalents (reprinted with kind permission from Ph. Courty and C. Marcilly, Rev. Ist. Franc. Pétrole, 39 (1984) 445. Copyright by Editions Technip).

Another general method was proposed in the seventies by Delmon and coworkers [36,37] which makes use of an α-hydroxyacid such as citric acid as complexing agent. Using about one equivalent of citric acid per equivalent of metal ion, and eventually ammonia, it is possible to dissolve almost every ion of the periodic table. Therefore, it is possible to mix the citrate solutions of different metal ions in the desired ratio, and then to concentrate the resulting solution by distilling off the water. The viscous product so obtained is homogeneous and transforms into a glassy and brittle substance which may easily be ground into a powder. The organic part may be decomposed by calcination, leaving a fine powder of oxides of the metal ions used with a high surface area.

This method has the advantage of starting from readily available salts of the desired metal ions, although the calcination of the organic part is best performed if nitrates are not used, because the decomposition in the presence of oxidizing ions such as Mn, Fe, Co, Ni or Cu may turn into a sudden, non uniform combustion or, in the case of Ag, explode.

Both the sol gel and the citrate methods are excellent for their ability to keep different elements inside the same structure; furthermore, since they do not involve any unit operation (for example a filtration) in which part of the metal ions may be lost, they lead to oxides of known composition (that of the starting solution).

5.3. Preparation of solid solutions and defect structures

The formation of solid solutions, although not characterized by specific preparation methods, significantly widens the possibility of comprising all the desired metal ions inside a single structure. Indeed it is known that many structures may host in a certain position more than one element [38]. Two solids having, in that position, two different elements are called isomorphous, and will display slightly different X-ray patterns. In particular, where the position of the diffraction peaks is concerned, due to the different steric requirements of the two elements, the two structures will have slightly different cell parameters. A solid containing both elements occupying in a more or less statistically random way the above mentioned position, is called a solid solution of the two isomorphous structures. It will be characterized by cell parameters which are intermediate between the values of the two isomorphs, according to the degree of the substitution of one element with the other, and therefore will display an X-ray pattern with position of the lines intermediate of those of the two isomorphs, and not the superposition of the spectra of the two isomorphs. The most stringent structural requirement for a solid solution to occur is the ionic radii compatibility.

An example of how isomorphous substitution may lead to phases comprising new elements and therefore to an unprecedented catalytic reactivity occurs in zeolites [39].

Another example of solid solution is the MoO_3-V_2O_5 system, which may be used for the selective oxidation of 1-butene to maleic anhydride and has a maximum of selectivity at about 25% MoO_3 which corresponds to the solubility limit of the oxides [40].

The situation is even more complex, but nevertheless open, for finding new possibilities of associating different elements inside a single type of structure, if one consider that the ions may significantly deviate from occupying only regular sites, enlarging the original definition of the structure and introducing different sorts of defects into it. It must also be considered that the possibility of building up a structure with a hard spheres model is a first approximation approach. Indeed ionic radii of the elements are not absolute values, but may vary according to the type of structure and site in which they are hosted [41]. It is beyond the scope of the present work to analyze all the different sorts of deviation from the regular structure and of the possible structural and electronic defects [42]: two examples only will be given.

Spinel related structures have several applications in catalysis, such as alcohol synthesis, are cubic and have as general formula A_2BO_4 with both octahedral and tetrahedral holes partially occupied. The effective site occupancy however may widely vary according to the nature of A and B, giving rise to a family of structures having at one extreme $ZnCr_2O_4$, in which all Cr ions are in octahedral holes and Zn ions in tetrahedral ones (normal spinel), and at the other extreme Fe_3O_4, which may be also written Fe^{3+} $[Fe^{2+}Fe^{3+}]\ O_4^{2-}$ in which all divalent Fe ion is in octahedral sites (inverse spinel).

The important role played by Bi and Te ions in promoting the selective ammoxidation of propylene to acrylonitrile in multicomponent oxide catalysts may not be explained by the formation of new phases, but by the presence of these ions in an interstitial 'irregular' position, inside the voids of the host structure in a high oxidation state and high coordination to lattice oxygen [43].

5.4. *Use of alloys and bimetallic catalysts*

Catalysis by metals has many important applications. One of the reasons for their success is based on the possibilities of the associations they offer, particularly when highly dispersed with particle size not greater than a few nanometers. Unfortunately all metallic catalysts tend to sinter. This phenomenon already starts during their formation by reduction and continues during the thermal treatments and use in the catalytic reaction, and generates a rapid decay unless the phenomenon is seriously contrasted, e.g. by an effective supporting. Some efforts to get to the root of the problem have been made, by avoiding the necessity of introducing a reduction step to obtain the dispersed metal. Small amounts of solvated metal atoms, which may be used in organic synthesis can be prepared by metal evaporation and low temperature trapping. When these weakly ligand stabilized metal atoms are gently warmed in presence of a catalyst support, an exceptional dispersion is obtained with unusual reactivity. These dispersed heterogeneous catalysts are termed solvated metal atom dispersed or SMAD [44]. Unfortunately this technique has not been developed to such a stage to obtain large amounts of catalysts to be used for high tonnage applications.

Alloys are solid solutions of different metals. Their association may offer a different reactivity in respect to the pure metals: nickel-copper, palladium-silver, palladium-gold are examples of alloy systems. A distinct difference between bulk and surface composition, which may also be a function of the particle size, is typical of alloys. The nature of the surface composition primarily determines the catalytic properties of an alloy. The surface atoms do not lose their individuality and the reactivity may be understood in terms of groups of surface atoms, although some long range effect may also be present. For example in some reactions performed on a Ni-Cu catalyst Cu may act as a diluent, since it may be considered rather inactive when compared to nickel. Ensemble effects may be observed, which will depend on the surface concentration and arrangement of Ni and Cu. Fig. 22 shows the activity of Ni-Cu alloys for the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene. The activities refer to reaction rates at 316°C. Ethane hydrogenolysis activities were obtained at cyclohexane and hydrogen pressures of 0.030 and 0.20 atm, respectively. Cyclohexane dehydrogenation activities were obtained at cyclohexane and hydrogen pressures of 0.17 and 0.83 respectively.

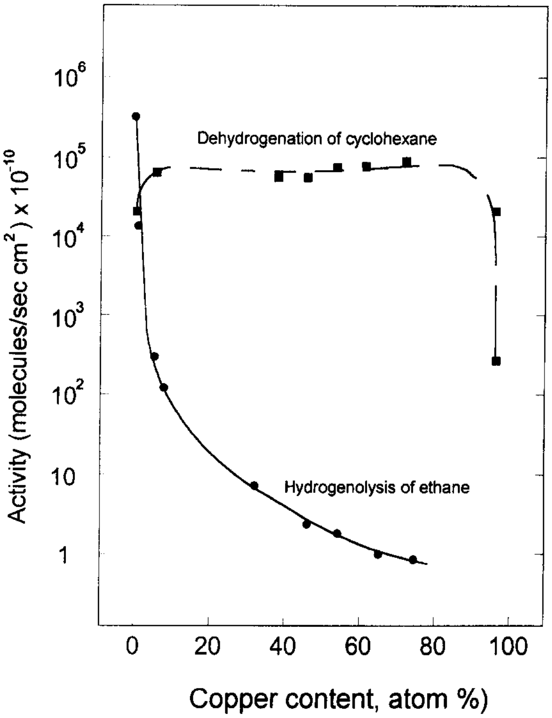

Fig. 22. Activities of Ni-Cu catalysts for the hydrogenolysis of ethane to methane and the dehydrogenation of cyclohexane to benzene [45].

The different trend of the two reactions may be explained by supposing that the carbon–carbon bond rupture involved in hydrogenolysis is sensitive to electronic and geometric surface factors, while cyclohexane dehydrogenation is comparatively insensitive to such factors [45].

Bimetallic catalysts are an aggregation of two different metals which may also be immiscible at the bulk scale. Pt-Re catalysts which were successfully introduced in reforming catalysts in the seventies are an example.

Platinum and rhenium have different crystal structures (fcc vs. hcp) and do not exhibit complete miscibility in the bulk [46]. However, these factors may have limited significance for highly dispersed metals. Moreover, during the reforming reaction the actual form may change, because Re may be present at the surface not in a zerovalent state, but in a sulfided state. The surface structure may be written ReS_{ads} which acts to divide platinum surface into very many small clusters of the size of 1 to 3 platinum atoms [47]. The platinum is partly in zerovalent form and partly as PtS_x and is adjacent to rhenium.

5.5. Preparation of supported catalysts

As already pointed out in Section 3 a way of improving the dispersion of the active species is to spread them on a support. The preferred preparation procedure starts from a preformed support because in this case it will impart its porous textures and mechanical toughness, and no further forming operation will be required. The active species are introduced into a porous support not in their final form but by impregnation with a solution containing a precursor, the choice of which is crucial for the final dispersion.

The impregnation will be called with no interaction when no specific interaction between the impregnating solution and the support is foreseen or no particular attention is given to following this aspect. In this case the greater dispersion of the active species observed for a supported catalyst must be ascribed to differences in the precipitation of the precursor occurring during drying. In fact, although the formation of the precipitate particles is ruled by the same laws for supported and unsupported catalysts, the heterogeneous nucleation is enormously enhanced inside the pores by the high surface area available of the support in contact with the solution. In the thermal treatments which follows the support acts as a 'spacer', i.e. keeps separated the small crystals formed and slows down the process of crystal growth (not the transformation into the final active species). The final dispersion depends on many parameters, such as support texture, precursor solubility and drying velocity and on the nature of the starting salts.

The interaction of the support with the active species is not only physical in nature, but there is always a more or less pronounced influence of its chemical nature. For example alumina, one of the most used supports, may often influence the chemical evolution of the supported active species or may even give rise to some sort of aluminates.

The impregnation with interaction tries to take advantage of a chemical interaction of the support with the impregnating solution so as to obtain a better dispersion of the active species: dispersion reaching almost the value of 1 (atomic dispersion) may be reached during this stage. The problem is to keep high values also in the following operations of drying, calcination, or reduction (in the case of metal supported catalyst). Often the particle size of a metal supported by this procedure is of the order of 10 Å, while by impregnation with no interaction it is rare to reach values below 50 Å [31].

In order to perform an impregnation with an effective interaction it is necessary to consider that true ion exchange reactions between ions of the precursor in solution and the surface of the

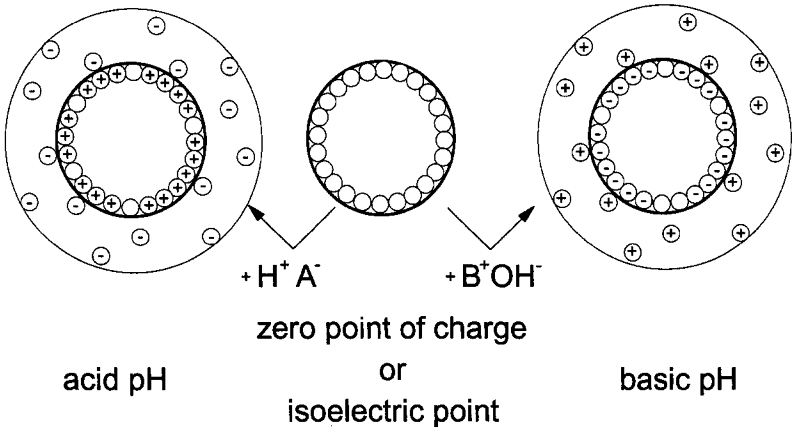

Fig. 23. Schematic representation of a surface polarization of an oxide particle as a function of the solution pH [48].

support occur during impregnation. These reactions are characterized by a kinetics and by equilibrium constants. The kinetics of exchange will in general be very fast for reactions highly favored from the thermodynamic point of view, and will lead to non-uniform distribution of the precursor inside the particle, because diffusion of the precursor inside the pores during impregnation will be a slow process compared to the ion exchange with the surface. In order to reduce the exchange rate and extension of exchange other ions may be introduced which may compete for the same site: e.g. Cl^- may be used as a competitor with $PtCl_6^{2-}$ in the exchange process.

Furthermore it must be considered that the surface of the support changes its polarization according to the value of the pH of the solution and to the isoelectric point of the solid [48]. Schematically the equation involved in the surface polarization may be written, in acidic medium (pH below the isoelectric point)

$$\text{S-OH} + H^+A^- \rightleftarrows \text{S-OH}_2^+A^-$$

while in a basic medium (pH above the isoelectric point) the equilibrium involved is

$$\text{S-OH} + B^+OH^- \rightleftarrows \text{S-O}^-B^+ + H_2O$$

The situation is depicted in Fig. 23 at pH below the isoelectric point the surface will be positively charged and will be surrounded by anions for simple electrostatic reasons and therefore the surface will attract and absorb anions, while at pH above the isoelectric point the surface will be negatively charged, will be surrounded by cations which, therefore, will be absorbed from the solution. To get information on the capacity of ion absorption, additional information on the evolution of the polarization as a function of pH is necessary. This can be done, for example, either by measuring electrophoretic velocity, or by neutralization experiments at constant pH. Since the isoelectric point of the support plays an important role together with the pH of the solution and the ionic species of the precursor, in Fig. 24 the isoelectric point of some oxides which may be used as supports are reported. Much of the irreproducibility which is frequently reported in the literature for supported catalysts must also be ascribed to the fact that these simple principles are not taken into consideration.

Oxide	I.E.P.S.	Adsorption
Sb_2O_5	<0.4	CATIONS
WO_3 Hydrous	<0.5	
SiO_2 Hydrous	1.0-2.0	
U_3O_8	~4.0	CATIONS or ANIONS
MnO_2	3.9-4.5	
SnO_2	~5.5	
TiO2 Rutile	~6.0	
Anatase		
UO_2	5.7-6.7	
γFe_2O_3	6.5-6.9	
ZrO_2 Hydrous	~6.7	
CeO_2 Hydrous	~6.75	
Cr_2O_3 Hydrous	6.5-7.5	
α,γ Al_2O_3	7.0-9.0	
Y_2O_3 Hydrous	~8.9	ANIONS
α Fe_2O_3	8.4-9.0	
ZnO	8.7-9.7	
La_2O_3 Hydrous	~10.4	
MgO	12.1-12.7	

Fig. 24. Isoelectric points of various oxides [48].

A uniform distribution of small particles over a support may be obtained also with the deposition–precipitation proposed by Geus [49,50]. In this method a metal solution containing urea is well mixed with the support powder at room temperature. Then the temperature is raised to 70–90°C, where the hydrolyses reaction takes place:

$$CO(NH_2)_2 + 3H_2O \rightleftarrows 2NH_4^+ + CO_2 + 2OH^-$$

The hydroxyls are produced homogeneously throughout the solution, preventing the formation of regions of high local pH. Since in the presence of an active precursor-support interaction, nucleation of the catalyst precursor at the surface of the support proceeds at lower concentration than those needed for precipitation in the bulk of the solution, precipitation exclusively on the support surface may be achieved.

5.6. Other methods for dispersing metals

Dispersed metals may be obtained by numerous other techniques of which we shall give only a few examples in this brief introduction.

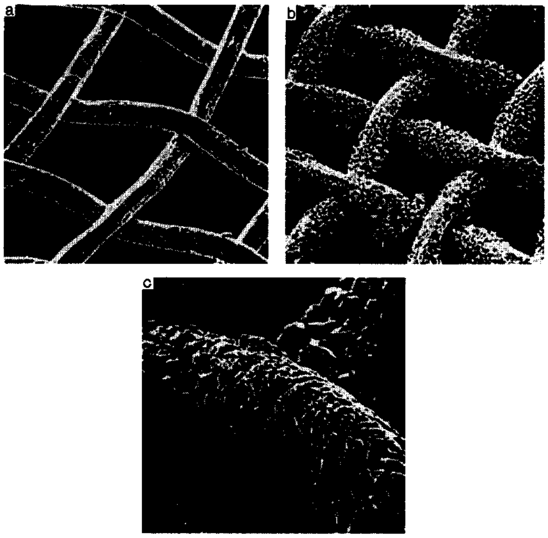

Fig. 25. Scanning electron micrographs of 10% Rh-90% Pt wire. (a) Original gauze as drawn, showing uniform grain structure and absence of nodules on the wires. (b) The gauze in part (a) after one-half the normal gauze life installed in a nitric acid plant, showing the nodular pattern typical of an active gauze. (c) An enlarged view of the crossover point of the two gauze wires in part (b) showing the characteristic octagonal crystal structure and nodules, which are concentrates on the wire surface between crossover points [Platinum Met. Rev., 15 (1971) 52].

As already mentioned the oxidation of NH_3 to NO is performed on Pt/Rh gauzes, i.e. on a catalyst which has no porosity to avoid internal diffusion limitations. The gauzes are laid one on the top of the other to form a pad about 5 mm thick containing as many as 40 gauzes. The standard is 80 mesh (31.5 wires per cm) woven from wire 0.003 in (0.075 mm) in diameter. This represents a reasonable optimum between the desire for fine wire and high area on the one hand and mechanical requirements on the other.

The substantial increase in activity which is initially observed is due to the increase of roughness of the woven wire which significantly increases the external surface, as shown in Fig. 25.

This increase of roughness of the wires, when powders are carefully eliminated from the gas flow, are ascribed to the reaction [51]:

$$Pt_{(s)} + O_2 \rightleftarrows PtO_{2(g)}$$

PtO_2 is slightly volatile and moves downstream where it may eventually be recovered in part.

Using a Pt/Rh alloy instead of pure Pt has as a consequence a surface enrichment of Rh [51]. Rhodium itself is slightly less active than Pt but much less volatile. Alloying Pt with 5–10% Rh therefore significantly reduces metal losses and increases the gauze life.

Finally we shall give two examples in which the catalyst particle becomes porous by the selective removal of some component.

The preparation of the ammonia synthesis catalyst starts from a melt obtained at about 1500°C and in an inert atmosphere of Fe_3O_4 Al_2O_3 and K_2O (2–5% each) plus small quantities of other promoters, which however are not essential. The melt is cast, allowed to cool and ground. At this stage Fe and Al are well interspersed in an oxide matrix, because they form a solid solution with spinel structure. The catalyst precursor is then slowly reduced, most frequently inside the reactor, in a gas circulating at the maximum possible rate, the temperature increase is controlled so that the water vapor concentration never exceeds 3000 ppm [52]. Although a substantial amount of oxygen is lost during this reduction process, the catalyst maintains its external geometrical dimensions, the oxygen loss generates a high surface area with small pores [53]. Collapse of the structure during reduction and reaction temperatures is prevented by alumina acting as a spacer.

The K_2O mainly acts as an electronic promoter, facilitating the dissociative chemisorption of N_2.

Nickel, copper and cobalt can be prepared in a form of pyrophoric highly reactive powders which can be used as catalysts in hydrogenation reactions to be carried out in slurry reactors, using the preparation proposed and patented by Raney in 1925.

This technique starts from an alloy – in the case of Raney nickel typically a 1:1 nickel aluminum alloy which is reacted with a 20% solution of sodium hydroxide, which leaches out much of the aluminum leaving Ni untouched. Some hydrated alumina is also formed and retained, which may act as a textural promoter.

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