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# PREPARATION OF HETEROGENEOUS CATALYSTS
## Synthesis of highly dispersed solids and their reactivity

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The preparation of heterogeneous catalysts has been for many years a dynamic field of sub-nanotechnology and remains so nowadays. The approach to preparation must be examined in function of the specific demands concerning (i) activity and (ii) selectivity, that both depend on the arrangement of atoms at a scale smaller than 0.02 nm. Adequate access of reactants to the surface must be provided. Most catalysts are used in the form of pellets or cylinders obtained by pressing, extrusion or other techniques. This implies a control of texture at dimension scales extending from a fraction of a nanometer to several millimetres (and sometimes more). A third demand (iii) is resistance to ageing. In particular, stability at relatively high temperatures is necessary.

The strategy adopted in the majority of cases is to start from a material that is homogeneous in composition at the Angström scale, generally a liquid or a solid of complex composition, frequently amorphous. A general objective is to locate the different constituting atoms at precise positions. The main difficulty is to transform the starting precursor into a highly porous solid without segregation of different elements that would produce tiny parts with different properties.

The specific approach to catalyst preparation is based on the general concepts used for controlling the reactivity of solids. Typical methods of general use will be examined. Chemical bonds of practically any kind can retain the elements constituting the future catalyst at the position they have in the precursor. The so-called 'citrate process' and its variants are of wide application. More elaborate approaches start from molecules or polymers associating the necessary elements.

**Keywords:** *catalyst preparation, citrate method, diffusion in solids, mixed oxide catalysts, multi-component precursors, prevention of nucleation, reactivity of solids, segregation in solids*

## Introduction

In a collective issue in honour of professor Boldyrev, a contribution concerning the synthesis of solid ('heterogeneous') catalysts certainly deserves a place. The present contribution must refer to a chapter of the Handbook of Heterogeneous Catalysis published in 1996 dealing with the same subject [1].

In modern chemical and petroleum refining industries, more than 90% of the new processes rest on catalytic mechanisms. The vast majority of industrial catalysts are solids. In comparison, the proportion of non-solid catalysts (liquids and gases) is very small, according to all criteria (mass, value, size of industrial plants, etc.): they are involved in between 5 and 15% of the catalytic processes. Solid catalysts often contain two or several solid components, different in composition, porosity, specific surface area, etc., that must be carefully controlled to obtain optimal activity, selectivity and stability in time during the catalytic reaction. A typical class of two-phase catalysts is constituted of an active phase deposited on a support, or carrier, possessing a low or, alternatively, a crucially useful catalytic activity of its own, associated with useful mechanical or other physical properties (strength, thermostability, heat conductivity…). A typical example is that of a noble metal highly dispersed on alumina or a silica-alumina mixed oxide, for hydrocracking or isomerisation in the presence of hydrogen. In such catalysts, the metal possesses the hydrogenation-dehydrogenating property, and the support carries acidic sites that permit isomerisation and some selective breaking of carbon-carbon bonds. Solid catalysts correspond to many different compositions as well as diverse structural and textural properties.

For suggesting the importance of the chemistry of solids and the role of a control of their reactivity, it will be sufficient to examine the typical case of oxides. Presently, probably more than 98% of the supports used for catalyst preparation are oxides. Oxides used with or without support constitute the largest proportion of the active materials. For the present article, it does not seem necessary to make a detailed list of the properties that a catalyst must possess. Concerning specifically supports, it is sufficient to say that they have the following roles:

(*i*) They permit a high dispersion of the supported phase. In newly prepared reforming catalysts, more than 50% of the platinum atoms are usually accessible

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to the reactants. The support must therefore possess a very high surface area.

(*ii*) The shape of the support, and especially the presence of tiny pores (of diameter 1–5 nm) often connected to a red of mesopores of 5–20 nm, allow an even diffusion of reactants and products to and from the inside of the catalyst pellets (diameter 0.1–10 mm).

(*iii*) The support must keep its structure and porosity for months or years at temperatures currently higher than 250°C, that often reach 750°C in many processes. Therefore it must be composed of refractory materials ($Al_2O_3$, Si–Al mixed oxides, barium hexa-aluminate…).

(*iv*) The composition of the support must be such that the desired reaction gets efficiently catalysed.

The teachings of ceramic science are useful for satisfying demand (*iii*), but completely different approaches are necessary for (*i*) and (*ii*).

It is clear that these demands also concern catalysts that are used without support. Table 1 mentions some of them. The catalysts of this category are crucial for the production of synthesis gas (CO conversion step) and energy conversion as well as in the manufacture of major intermediates in chemistry. Another family of oxide materials, but of more complex composition, structure and texture, play a key role in the petroleum refining industry (catalytic cracking, for example with zeolites) and in chemistry (selective partial oxidation of hydrocarbons).

Catalysis is a very complex process. The catalytic action consists in accelerating a useful reaction at the expense of other thermodynamically possible transformations. For saving energy and raw materials, catalysts must be extremely selective. This requires that surface composition be very precisely adjusted at the scale of the elementary catalytic process, that is at the scale of molecules. This is necessary for the different surface atoms to work in co-operation with each other (demand (*iv*) mentioned above). Consequently, one of the major challenges in catalyst preparation is to synthesise highly dispersed solids (high surface area per unit mass of material) with a composition uniform at the atomic scale. This demand is far from being satisfied for catalysts and supports, neither in the laboratory nor in fabrication plants. Nanotechnology certainly goes in the direction of the goal, but, as will be suggested in this contribution, other advanced concepts like molecular recognition will have to be used. Catalysts demand not only nano-scale but also Angström-scale control.

A typical example is that of a widespread group of materials, namely mixed oxides containing silicon and aluminium. These silica-aluminas are catalytically active. Used as supports for metal sulfides that possess complementary catalytic properties, they command the transformation of more than 1 Gton/year of various intermediate products in the very first steps of petroleum refining. Angström-scale homogeneity is crucial, because the acidic sites present of the surface associate Si, Al and O atoms in precise proportions to create the proper atomic arrangement determining the nature (Brönsted or Lewis) and strength of the catalytic sites, and hence selectivity.

The fact that the demands for small scale composition homogeneity are not yet satisfied can be very easily illustrated in the case of coprecipitated samples, where pure silica is very frequently observed and considerable fluctuations of the Si/Al ratio by factors of 2 to infinity are measured over a distance of several tens of nanometers for the best, and several micrometers for most samples [2–4].

This is illustrated in Figs 1 to 4, taken from data obtained with 17 different samples. These samples were prepared by either (*i*) co-precipitation where a solution containing salts of both elements was mixed with a base or (*ii*) by the sol–gel method, in which a mixture of alkoxides is hydrolysed. The heterogeneity comes from the different reactivity of the starting salts or, respectively, alkoxides [4]. The laboratory samples came from the same laboratory using always the same procedure (*ii*) [3]. With respect to the industrial samples, most of them were probably obtained by co-precipitation, but perhaps some of them using sol–gel or modified sol–gel techniques. In these investigations, the samples were dispersed in water with an ultrasonic vibrator. A drop of the resulting suspension was deposited on a thin carbon film supported on a standard copper grid. After drying, the samples were observed and analyzed by transmission electron microscopy (TEM) on a JEOL-JEM 100C TEMSCAN equipped with a KEVEX energy dispersive spectrometer for electron-probe microanalysis (EPMA). The accelerating potential used was 100 kV. The first observations concerned the general aspect of the sample, looking at the whole grid. Then, different points of each particle were analyzed (2 or 3); the same procedure was used for the analysis of a total of 10 to 25 particles for each sample. The diameter of the static spot was 0.2 μm. The duration for each analysis (accumulation) varied between 60 and 240 s. The procedure is reported in detail in [4].

On the whole, the samples prepared according to the original sol–gel method (from alkoxides) in the laboratory are more homogeneous, but one sample (14.8% $Al_2O_3$, Fig. 14a of [4], not represented here) contained particles of pure silica. Except perhaps for compositions around 25%, the degree of heterogeneity was similar for all sol–gel samples. It is understandable that industrial silica-aluminas examined in identical ways can exhibit substantially different degrees of homogeneity (Fig. 4).

The necessity to have more than one component in a catalyst arises from many needs. Those linked to polyfunctionality, often required for the different steps in a reaction, were mentioned in the preceding paragraphs. Other reasons are the need to enhance the rate of some reaction steps and to inhibit unwanted side reactions, the wish to increase thermal stability, and the necessity to take advantage of observed synergetic effects. From a fundamental point of view, the presence of several metal elements in a common structure permits the adjustment of the local electronic properties, imposes well defined coordinations,

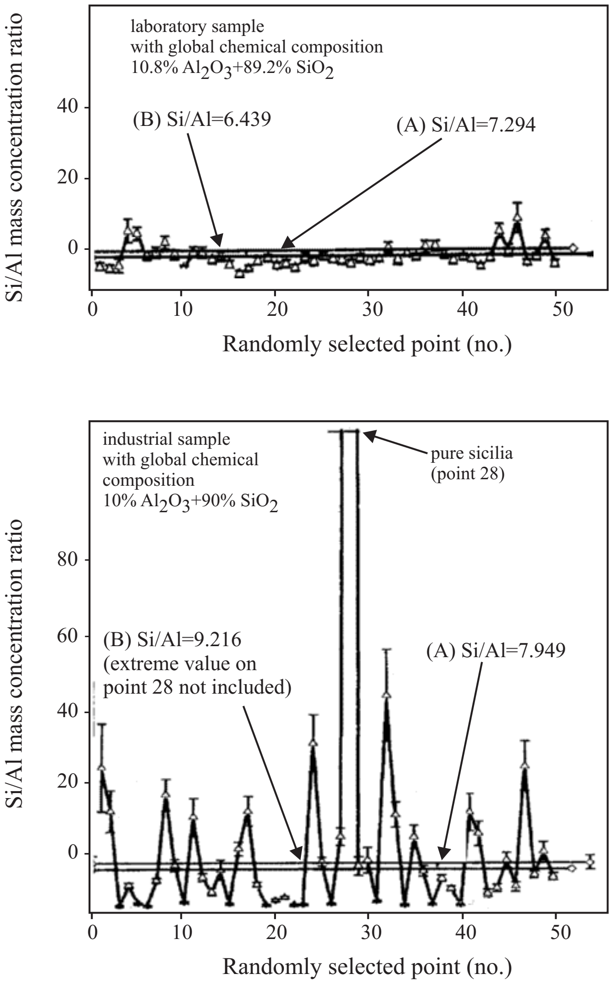

**Fig. 1** Nanoscale fluctuations of the Si/Al mass concentration ratio for laboratory and industry prepared samples of alumina content around 10% (Similar data were obtained for Si/Al around 5% or 50–60%). *A* – Si/Al calculated on the basis of the global silica and alumina contents. *B* – the average value calculated from the Si/Al ratios experimentally measured on all the analyzed points (except for the extreme values, that coud not be taken into account for calculation). Please see the text for the physical meaning of the *A* value [4]

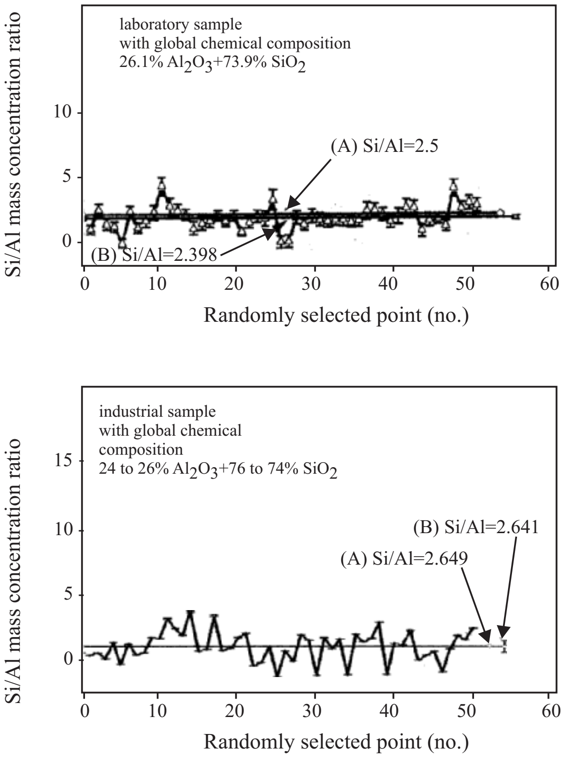

**Fig. 2** Nanoscale fluctuations of the Si/Al mass concentration ratio for samples of alumina content around 25–26%. Please see the legend of Fig. 1 for remaining details [4]

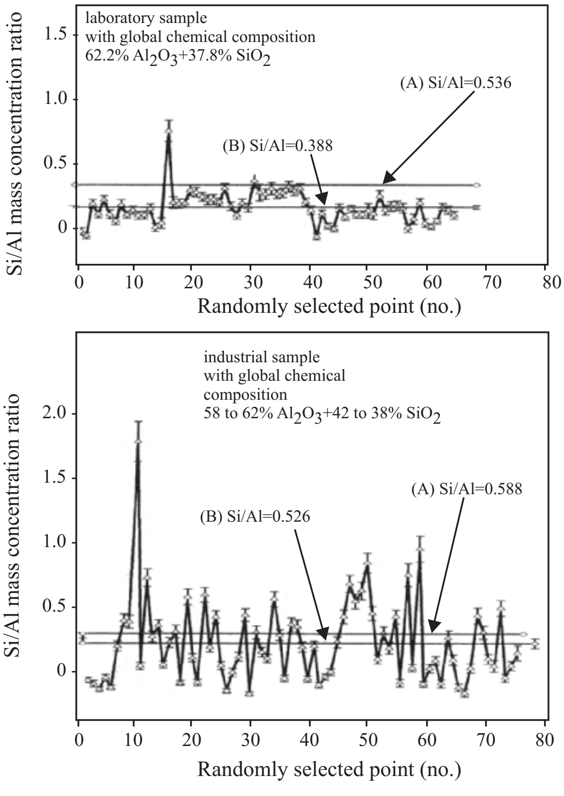

**Fig. 3** Nanoscale fluctuations of the Si/Al mass concentration ratio for samples of comparable contents of silica and alumina. Please see the legend of Fig. 1 for remaining details [4]

limits the extent of oxidation–reduction phenomena, and may stabilize the whole catalyst by retarding sintering. Mixed oxide catalysts are used as such, or as precursors of active catalysts, for a whole range of important industrial processes, a representative selection of which was given in Table 1.

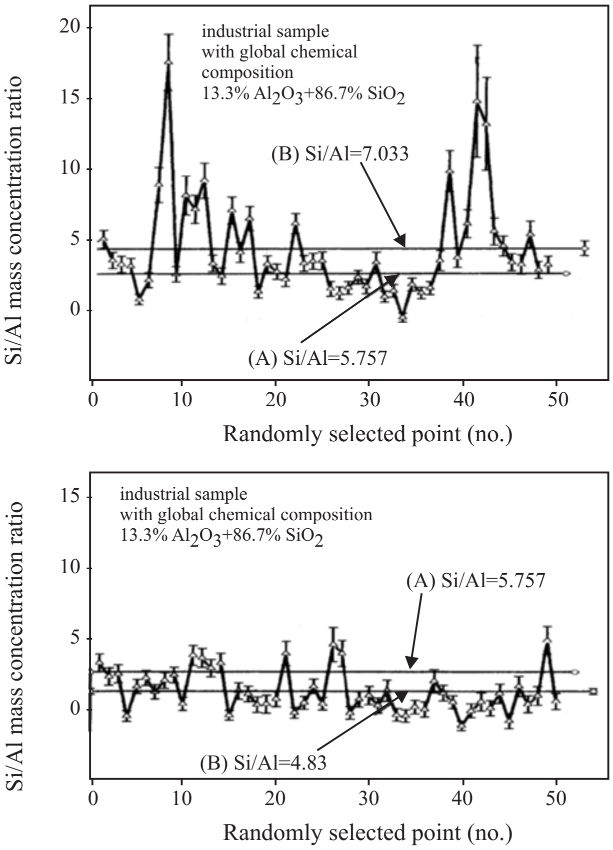

**Fig. 4** Differences in nanoscale fluctuations of the Si/Al mass concentration ratio between batches for industrial samples of identical composition. Please see the legend of Fig. 1 for remaining details [4]

Preparation of atomically homogeneous multi-component catalysts by conventional methods, however, is often difficult due to three main reasons:

(*i*) Deposition of active precursors either as a precipitate or onto a support often gives separate moieties, instead of a single phase of uniform chemical composition.
(*ii*) Segregation of the active components can occur during the thermal treatment of the catalyst precursor.
(*iii*) The support can selectively interact with one of the active components at one or the other stage of the formation of the mixed oxide.

A good example of the latter case is the reaction of iron with silica in silica-supported iron molybdate, a fact which made impossible the use of silica as a support in the case of catalysts used for the oxidation of methanol to formaldehyde. Some of the methods to overcome these difficulties in catalyst preparation will be discussed in this contribution.

**Table 1** Some important mixed-oxide catalysts used in industry

| Catalyst | Active phases | Industrial processes |
|---|---|---|
| Copper chromite | $CuCr_2O_4$ | CO conversion (low temp.), oxidations, hydrogenation, hydrogenation-hydrogenolysis |
| Zinc chromite | $ZnCr_2O_4$, $ZnO$ | methanol synthesis (high pressure) |
| Copper/zinc chromite | $Cu_xZn_{1-x}Cr_2O_4$, $CuO_y$ | methanol synthesis (low pressure) |
| Iron molybdate | $Fe_2(MoO_4)_3$, $MoO_3$ | methanol to formaldehyde |
| Iron oxide/potassium oxide | $KFeO_2$, $K_2Fe_{22}O_{34}$ | ethylbenzene to styrene |
| Bismuth molybdate, other oxides+promoter oxides | mixed oxides: Mo, Bi, Sb, Sn, Co, etc. | propene to acrolein propene to acrylonitrile |
| Zinc ferrite | $ZnFe_2O_4$ | oxidative dehydrogenation |
| Vanadia-molybdena | $V_2O_5$–$MoO_3$ solid solution | benzene/butene to maleic anhydride |
| Vanadium phosphate | Mixed $(VO)_x(PO_4)_y$ | butane to maleic anhydride |
| Chromia -alumina | $Cr_xAl_{2-x}O_3$ | dehydrogenation of light alkanes |
| Mixed oxides | perovskite type | catalytic combustion |
| Barium hexaaluminate | $BaAl_{12}O_{19}$ | catalytic combustion (support) |

## Outline of the general approach

In all cases, the objective is to slow down the processes able to let species migrate to form unwanted compounds or to allow them to segregate when homogeneous mixing at the atomic level is desired. In principle, when atomically homogeneous mixtures are desired, gases or liquids are ideal precursors. Practically, liquids are more convenient. The reason is that the ordinary liquid state has no long-range structure, and hence permits a statistical repartition or distribution all over the volume of its contents at the molecular scale. However, segregation almost invariably occurs when liquids are reacted to give solids (e.g. by precipitation, because one element usually precipitates before the other component or components [5]). The fundamental reason to use of solid-state reactions is that, unlike in a liquid, the diffusion of atoms or ions in a solid is very difficult and it is practically frozen at relatively low temperatures. Figure 5 is a schematic representation of the situation inspired by the theory of the transition state. The ‘activation’ necesssary for movements in the liquid state is of the order of magnitude of Van der Waals forces or hydrogen bond strength, that is a few $\text{kJ mol}^{-1}$. Diffusion in solids necessitates the losening of ionic forces or the breaking of covalent bonds, the strength of which amounts to several tens to hundreds of kJ/mole. A very crude estimation of the relative rates of the two kinds of processes with the background of the transition state picture shows that rates of reactions differ by several orders of magnitude. An additional reason is that nucleation, by favouring the formation of new phases, necessitates preliminary diffusion steps. Whenever a solid of complex composition cannot be obtained by a direct reaction, an indirect method can be tried. The situation is similar if the reaction of a supported catalytic material with the support must be avoided. In both cases, all steps in the preparation that could facilitate diffusion should be avoided. This is discussed in more details in a chapter of the Handbook of Heterogeneous Catalysis [1]

In a general way, blocking or hindering diffusion may be achieved

- by making physical diffusion slower,
- or by ‘pinning’ the various species in their initial location in a liquid by relatively weak links (e.g. van der Waals forces, ionic forces…)
- or by blocking all partner at their initial position by chemical bonds.

Actually, a wide spectrum of methods exist for those purposes. Consequently a perfect classification is nearly impossible.

It may be noticed that a few catalysts are obtained from solid precursors by topotactic reactions (e.g. from solids of hydrotalcite structures). The starting compounds are mainly hydroxides, carbonates, or oxalates. The key step in preparation is therefore that of the precursor, rather than that of the catalyst itself. This is possible if a solid can be obtained of a chemical nature which differs from that of the desired solid (e.g. a hydroxide, salts of organic acids, etc.), but which contains the metallic elements in the proportion required by the catalyst. The key reaction is then the solid-state transformation of this hydroxide or salt to the desired oxide. Keeping the material in the solid state throughout the transformation permits a powerful control that prevents all unwanted atomic restructuring in the bulk during catalyst preparation. Solid-state chemistry, more precisely topochemistry (‘chimie douce’), offers the additional advantage that specific structures and even textures (as for the layers of phyllosilicate in pillared clays) can be preserved intact throughout these solid-state transformations. The following discussion also covers this case.

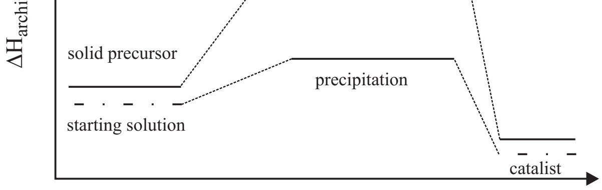

**Fig. 5** Schematic representation of the approximate levels of formal activation energy in diffusion in fluids (liquids) and solids

Actually, the potential of processes starting from solid precursors is broader. Sometimes a single starting phase gives solid products containing two or several phases, each of them very highly dispersed and in intimate contact with each other. This was observed in catalyst preparation. On the other hand, identification of synergetic actions between catalyst components progressively convinced catalysis scientists that the synergy actually corresponded to a co-operation between distinct phases (initially called ‘remote control’ [6–8], namely control of the catalytic properties of one phase by signals, coming from a distinct phase). This is typically the case of many oxidation, ammoxidation and related processes. The techniques based on the decomposition of solid precursors can provide intimate mixtures of phases in close contact with each other. This enhances the efficiency of phase co-operation because the signals need to travel only on short distances [9]. This occurs spontaneously in the preparation of the so-called ‘iron molybdate’ (for the oxidation of methanol to formaldehyde), which is an intimate mixture of $MoO_3$ and iron molybdate, but can be controlled for obtaining better catalysts. Antimony oxide is essential in many selective oxidation reactions. The use of solid precursors very likely produces highly dispersed $Sb_2O_4$ in intimate contact with the other component.

Now, considering both highly dispersed solids of uniform composition at the atomic scale and mixtures of intimately interdispersed phases, it must be noted that the use of solid precursors offers an important additional advantage. The transformation of solids usually allows an efficient control of the texture of the solid products that other processes do not allow. An adequate selection of reaction conditions leads to highly dispersed solids possessing a defined porosity. The preparation methods described in the present section are cases that can be considered as typical, and have been selected to highlight (*i*) possible goals that can be reached and (*ii*) procedures used for reaching them.

The approach to catalyst preparation using solid precursors must take account the specificity of catalysts as product of the reaction compared to other solid materials. A difficulty rests in the fact that transforming a solid material to another may need a relatively high temperature. The migration of a constituent inside the structure of a solid involves an activation energy barrier to be overcome (Fig. 5). The Tammann temperature (taken approximatively as half the melting temperature in K) is generally believed to be that over which the atoms or ions in the bulk are sufficiently mobile. The temperature for decomposition of the solid precursor must therefore be lower than this Tammann temperature. The demands are still higher for obtaining a material of high surface areas as catalysts are. The Hüttig temperature (about one-third the melting temperature) is enough to make surface species sufficiently mobile to undergo sintering or lead to particle agglomeration. The conclusion is that the reactions considered in this article must occur at moderate or low temperatures, namely below the Tammann and Hütig values. These will generally be endothermic decompositions to solids and gases.

General surveys of solid-state reactions involved in catalyst preparation or production can be seen in Courty *et al.* [10–12], Courty and Marcilly [13, 14], and Delmon and de Keyser [15]. Several aspects of this subject are also covered and updated in the Proceedings of the International Symposia on Scientific Bases for the Preparation of Heterogeneous Catalysts, held in 1975, 1978, and then every 4 years at Louvain-la-Neuve, Belgium [16–24].

These solid-state reactions are based on concepts pertaining to the science of the reactivity of solids. Many of them were developed by Boldyrev, French scientists (kinetics of the transformation of solids, topotactic reactions, ‘chimie douce’), many other scientists in the world, and the present author [25–27]. Other fundamental aspects concerning nucleation due to supersaturation of species present in liquids and the role of surface energy (Gibbs–Thomson law) that tends to diminish dispersion and surface area are discussed in the relevant literature see, for example, [1]) and reviews by Marcilly [13] and Marcilly and Franck [14].

## Preparation methods: general

In conformity with the title of this contribution, the objective is to describe approaches to catalyst preparations using solid precursors. This excludes in principle coprecipitation and the original sol–gel method, widely used in ceramic and materials science. Only specific cases will be examined.

For reasons mentioned at the beginning, the presentation essentially concerns oxides, by far the most frequent case. For other catalysts (examples are: carbides [28], nitrates [29, 30], oxynitrides [31], phosphides [32]), mixed oxides usually serve as precursors and homogeneity is still more crucial. Even bimetallic catalysts have been prepared by reduction of precursors made by techniques presented in this section [33].

Several cases need to be distinguished when an atomically homogeneous multi-element catalyst is required:

(*i*) Direct preparation by various types of reactions (e.g. precipitation). There are very few examples. In practice, when using precipitation, perfect homogeneity is only possible if an oxoanion, e.g. a molybdate or a vanadate, reacts with a cation to produce the precipitate. The stoichiometry is dictated by the chemistry of this reaction and has little flexibility.
(*ii*) A two-step process, through preparation of another type of homogeneous solid of exactly the same composition (e.g. carbonate, hydroxide, oxalate or other precursors, for making finally an oxide) and, in a second step, thermally activating a solid-state reaction of this precursor.
(*iii*) Preparation of a solid approximately homogeneous followed by solid-state transformation, hoping that a higher homogeneity will be achieved during a second step.

The first category correspond to very specific cases and do not need special comments. Here, attention is given to both other categories. The discussion is organised according to the technique used.

A general comment has to be made here. The strategy consisting of starting from a homogeneous solid precursor and transforming it to the desired catalyst is only successful if diffusions in the solid state potentially leading to segregation are made difficult. This requires that only precursors decomposing to the final solid at low temperature, below the Tammann or Hüttig temperatures, be used. On the other hand, for reasons that cannot be presented here in full detail, it is advantageous that the solid precursor decomposes with production of large quantities of gases. In practice, hydroxides, carbonates, hydroxocarbonates, nitrates, and salts of carboxylic acids (formates, oxalates, acetates, citrates, etc.) satisfy both requirements. The main reason is that a coupling between the solid-state transformation and the formation of pores is necessary and the formation of pores is obviously promoted by the evolution of gases. Coupling effects in catalyst preparation are discussed in several articles [25, 27, 34].

One can essentially distinguish two steps in the procedure: the preparation of a homogeneous solid precursor and the careful decomposition of this precursor to the oxide. For the first step, it is crucial to avoid the segregation of the oxide species into separate solid phases. This is usually achieved by:

(*i*) Physical methods such as evaporation to dryness, drying by vaporization, freeze-drying, and crystallization. For the reasons explained above, the operation should be extremely rapid.
(*ii*) A physico-chemical method like some gelation methods.
(*iii*) Chemical methods such as precipitation, coprecipitation, oil-drop, oil-up, and complexation. Oil-drop and oil-up involve processes pertaining to categories (*ii*) and (*iii*).

This reflects the classification concerning the methods mentioned at the beginning, that can be used for slowing down diffusion processes.

However, the considerable development of heterogeneous catalysts has led to innumerable variations around the most frequently used techniques and combinations between techniques: micro-emulsions+oil drop, supercritical precipitation [19, 20], impregnation of high surface area solids that can be later eliminated by combustion, complexation+ spray-drying, etc. [16–21, 34–37]. We shall adopt a classification based on the techniques, rather than on fundamental mechanisms of action.

## Dry methods

One common method to prepare mixed-oxide catalysts is to grind or ball-mill them together, either dry or in a wet slurry; this is followed by calcination to temperatures of 600–1000°C. The operation may be repeated several times. In the past, catalysts for the styrene process were generally prepared in this way from KOH and oxides of Fe and Cr and other (proprietary) promoter components. The solid-solid reaction during calcination can be accelerated by ‘priming’ or catalyzing by a small amount of the product premixed with the reactant oxides, presumably for nucleating the desired phase. Ammonia synthesis catalysts which are prepared by mixing the components in the molten state do not pertain to this section, strictly speaking. A ‘fluid energy mill’, operated with steam injection at 400–700°C and 5–15 bar steam pressure, is applied in some cases. Some other techniques, used only rarely, are dry chemical oxidation of alloys, and electrolytic deposition. In general, the dry methods mentioned in this section give solids with a low surface area.

## Wet methods

### *Coprecipitation*

The most common method for mixed-oxide catalyst preparation is crystallization or precipitation or coprecipitation in solution of a precursor form (hydroxide, oxide, insoluble salt) of the catalyst [1]. Other specific steps, for example either addition of an extra component or its removal by partial extraction, may sometimes be necessary to adjust the final catalyst composition and ensure homogeneity.

One of the most studied cases was that of hydroxo-carbonates used for preparing catalysts containing copper and zinc or chromium with additional elements (e.g. Co or Al). These catalysts are used for making synthesis gas and methanol. The precursors are mixed compounds with flexible composition [12] with the following structures: hydrotalcite $M_6^{2+}M_3^{3+}$+$(OH)_{16}CO_3\cdot4H_2O$ (*M* representing metals of valence 2 or 3), malachite $Cu_{2-x}^{2+}Zn_x^{2+}(OH)_2CO_3$ and auricalcite $Cu_{2-x}^{2+}Zn_x^{2+}(OH)_6(CO_3)_2$ [12, 38–41].

Precipitation (or simple crystallization) involves two main steps, nucleation and growth [12, 13, 42–47]. At the nucleation stage, very small crystals of the solid phase are formed; these have a high specific surface area and high surface energy, and hence are unstable. Below a certain critical nuclei size, the free energy of formation of the solid phase is less than its surface energy and the new phase is thermodynamically unstable. Above this critical size, the solid particles can grow. According to the conditions, this growth step is mainly controlled by interface or diffusion phenomena. The first case generally corresponds to the formation of complicated solid structures. The second is more common in the precipitation processes used in catalyst preparation. An overview is given in references given previously [5, 12–14]. An excellent detailed treatment of nucleation and growth phenomena can be cited [48]. Only more general statements or rules of thumb can be given here.

For nucleation:

(*i*) the higher the supersaturation, the higher will be the nucleation rate and, hence, the smaller the nucleus size;
(*ii*) any interface may play the role of a heterogeneous nucleus by lowering the surface free-energy of the new phase, and thus increase the rate of nucleation;
(*iii*) in general, higher temperatures lower the nucleation rate by increasing the critical size of the nuclei -

the upper left boundary of the homogeneous nucleation band reflects this trend.

For growth:

(*i*) the higher the supersaturation, the higher will be the growth rate, but it is rapidly limited by diffusion processes;
(*ii*) since an increase of temperature enhances the diffusion rates, the higher the temperature, the higher will be the growth rate of the new phase.

Obtaining a highly dispersed precipitate therefore necessitates the folllowing conditions:

(*i*) A vigorous stirring of the solution while adding the chemical compound, that triggers precipitation. This is beneficial in two ways: first, each elementary volume of solution reaches rapidly the highest degree of supersaturation; second, it comes into contact several times with the agitator and the walls of the vessel, thereby also promoting heterogeneous nucleation by particles detached from the walls.
(*ii*) A rapid addition of the precipitating agent ensures a rapid reaching of the highest degree of supersaturation in the whole volume of the solution, hence a maximum nucleation rate is obtained. For the same reason, the best precipitating agent is the one giving the precipitate with the lowest solubility product.
(*iii*) Although the situation may be very different from case to case, precipitation is often advantageously made at the lowest practical temperature, as this often favors nucleation over growth.
(*iv*) As recently demonstrated in the case of $Ce_{1-x}Zr_xO_2$ solid solutions, crystalline mixed oxide nanoparticles can also be obtained by hydroxide coprecipitation followed by redispersion in an aqueous medium by sonication, using nitric acid as peptizing agent [43].

The multi-element product of precipitation may be an insoluble single compound, for instance $BaTiO_3$ (precipitation of a hydrated oxalate, $BaTiO(C_2O_4)_2\cdot 4H_2O$, and its thermal decomposition) or, cerium zirconyl oxalate corresponding to the stoichiometry $Ce_2(ZrO)_2(C_2O_4)_5$ to serve as precursor for $CeO_2$–$ZrO_2$ solid solutions [44]. It may also be a single-phase solid solution or a single-phase mixed structure, as in the precipitation by sodium carbonate of aluminates or hydroxoprecursors of aluminates of Cu, Fe, Ni, Zn and Mg. Divalent metal oxalates can also be precipitated in this way [45]. A third possibility is that metals precipitate more or less simultaneously, but in separate phases, e.g. metal hydroxides precipitated by NaOH, KOH and $(NH_3)$aq. Normally, aqueous ammonia is preferable for precipitation, especially when washing off all alkali from the catalyst is a prerequisite for the preparation of the final catalyst. An exception to this is when $(NH_3)$aq can form ammine complexes as with many transition metals (Ni, Co, Cu, Zn). Tables 3 to 7 in [1] presented non exhaustive lists of mixed salts which had been claimed to be obtained by coprecipitation.

### *Spray drying, spray calcination*

Spray drying is a versatile method that can produce mixtures of phases with a high degree of interdispersion and a relatively high degree of homogeneity, although there is, in principle, no atomic level homogeneity. Very often, slow evaporation of a homogeneous solution of two precursor salts, for example $MgSO_4$ and $Al_2(SO_4)_3$, leads to segregations of the two salts in the solid product. To prevent this, it is advantageous to eliminate rapidly the solvent, either by spray drying or hot petroleum drying. Spray drying is also frequently used for removing water when the active phase or the desired precursor has been produced. In certain cases, the temperature in the equipment can be raised enough to permit the reaction between the salts to produce an oxide combining two metallic elements. This may be called spray-calcination. The respective sulphates were used to make highly dispersed $MgAl_2O_4$ solid solutions. The success of the method, in this case, consisted in the very small size of the crystallites obtained by rapid drying and their excellent interdispersion, this promoting solid-state reactions at higher temperatures. This technique is used industrially to produce powders for the fabrication of ceramics [46]. Mainly single-metal oxides are made in this way, but it is claimed that $MnFe_2O_4$, $NiFe_2O_4$, $NiAl_2O_4$, dopant-stabilized zirconium oxide and titanates used as catalysts can also be obtained. Powders of surface area up to 20 $m^2\ g^{-1}$ can be produced. The powder is usually in the form of aggregates of 0.2–0.4 μm in the best cases, but often of over 100 μm in diameter [46].

By use of this technique, it is possible to prepare fine spherical catalyst particles in the 10–100 μm diameter range, as required for typical fluidized-bed catalytic processes. This is used for large-scale catalyst manufacture, the feed being generally a dilute hydrogel or sol that is sprayed from the top of a tower when hot air is blown in a cocurrent or countercurrent direction to dry the droplets before they reach the bottom of the tower. The fine droplets are produced or atomized by pumping the hydrogel or sol under pressure either through nozzles, or onto wheel discs rotating at a high speed. The method is also convenient to embed crystalline particles of micrometer or submicrometer size in an amorphous matrix of 10–100 μm diameter. The best known examples are the techniques to embed multicomponent bismuth molybdates in a 50% silica matrix for ammoxidation of propene to acrylonitrile, or to incorporate <1–3 μm zeolite crystallites in an amorphous silica-alumina/clay matrix for fluid catalytic cracking (FCC) catalysts. The use of spray drying or spray calcination for making atomically homogeneous mixed oxide slowly emerges from the development stage. Flame spray pyrolysis of precursors mixtures was recently shown to provide Pt/ceria-zirconia materials exhibiting higher specific surface areas than the conventional catalysts obtained by precipitation or incipient wetness impregnation [47].

### *Hot-petroleum drying*

Hot-petroleum drying constitutes an alternative to spray drying. It was developed by Reynen and Bastius [48], initially for small-scale preparations. However, the development of what industry improperly calls the sol–gel method, namely integrated conventional precipitation and gelling, makes it now a large scale preparation method. The principle consists in dropping a fluid material containing the active elements in kerosene. This fluid material may be a gel, a solution in the course of becoming a gel, a stabilized emulsion of a salt solution and kerosene, or an aqueous solution of salts. The temperature of the kerosene bath is maintained at about 170°C. The kerosene bath may be vigorously agitated if necessary. The water evaporates and the powder or, according to processes, the small solid spheres obtained are easily filtered and dried at around 250°C. The product is a free-flowing powder consisting of a homogeneous mixture of salts. The hot-petroleum drying method, contrary to the spray-drying variant (that we previously called spray calcination) does not permit the development of the solid-state reactions necessary to form oxides, but the highly dispersed and intermixed salts can be thermally decomposed without phase segregations. Just as spray drying, this method is also dependent on the evaporation of water being faster than the segregation phenomena. The controlling factors are thus the temperature of the hot kerosene and the rate of water evaporation from the droplets. The advantages of this method are the simple setup, the fact that kerosene can be recycled, and the lower energy consumption than for spray drying.

### *Freeze-drying*

Freeze-drying corresponds to the same purpose as both above-mentioned methods, but the strategy is different. In order to limit segregation, the action now concerns directly the physical diffusion process, that is slowed down. This can be achieved either by rapid cooling (freeze-drying) or by increasing the viscosity of the solution (by some of the methods described below, addition of hydroxycellulose or gums, for example). This increase of viscosity also plays a role in the more elaborate amorphous citrate process described later in this contribution.

Undercooling is the driving force in freeze-drying. An aqueous salt solution is introduced dropwise into an immiscible liquid (hexane or a petroleum fraction such as kerosene) cooled below –30°C. The individual droplets are frozen instantaneously and the solid particles are decanted or filtered. The frozen liquid often has a glassy structure. It is sublimed in a vacuum to obtain a homogeneous powder of fairly uniform particle size. Important parameters in freeze-drying are cooling rate and the final temperature of the solidified solution. These can be controlled to some extent, but only on a small scale. Hence the method is not very well suited to large-scale manufacture of catalysts.

## *Gel formation and chemical complexation methods*

### General comments

It is not useful, except for the sake of very fundamental interpretations, to make a strong distinction between methods resting on gel formation and those making use of chemical complexation. The reasons are (*i*) that the first ones, when used in isolation, are not very effective, and (*ii*) that the chemical complexation methods lead to the formation of solids or solid-like materials (or even real solids), so that making a clear separation is difficult and sometimes artificial. In the following, only important approaches will be mentioned, and the physico-chemical aspects of these methods will be emphasized.

Quite generally, the methodology for preparing finely divided heterogeneous catalysts also benefits from the development of the so-called ‘soft chemistry’ strategies implemented for the synthesis of multi-component inorganic materials. In that context, ‘precursor’ routes based on the thermal decomposition at rather low temperatures (below 500°C) of suitable precursors containing organic groups are widely used. This concerns the synthesis of oxides. Sulfides, nitrides or carbides can be obtained in a similar way, either starting with appropriate precursors, or by adapting the decomposition medium. Because these routes allow the formation of crystalline or amorphous solid substances under conditions significantly milder than those employed in conventional solid state synthesis (‘ceramic method’), the final materials often present relatively high surface areas. To select the appropriate temperature for the decomposition process, the thermal degradation scheme of the starting materials must be taken into account to find a compromise between the obtention of high surface areas and the extent of residual carbonaceous contamination. However, in most cases, when precursors containing only carbon, oxygen and nitrogen are used, the choice of appropriate conditions allows finely divided materials with very high surface purity to be obtained.

Two major classes of precursors are encountered. On the one hand, well-established methods are based on the use of polymeric precursors of ill-defined stoichiometry at the molecular scale, containing the desired metallic elements in appropriate amounts, together with a sacrificial matrix that ensures the efficient mixing at the molecular level. The widely used 'citrate methods' belong to this category, although in some cases (Al [49], Ti [50], V [51], Mn [52], Co [53], Mo [54], La [55]), well-defined citrate complexes could be recently identified and crystallized. On the other hand, in some other cases, coordination compounds with precise stoichiometries can be obtained, and even characterized from the structural point of view when crystals are produced. The presence of bridging and/or chelating organic ligands in these precursors was shown to avoid metal segregation during oxide formation. Carboxylates and polyaminocarboxylates like EDTA (ethylenediaminetetraacetate) or its heavier analogs like DTPA (diethylenetriaminepentaacetate) or TTHA (triethylenetetraminehexaacetate), give rise to a wide variety of such complexes [56–58]. More particularly, when different metals are involved in the formulation of the final oxide, the main advantage of these routes is the potential use of heterometallic single-source precursors, because they provide a much greater control on the metal stoichiometry in the final oxide. In particular, several examples of alkoxysiloxy metal complexes or other siloxane compounds have been described as precursors to silica-based multicomponent oxides containing for instance magnesium, chromium [59], molybdenum [60, 61], tungsten [62], vanadium [63], or zirconium [63]. Ideally, when bulk mixed oxides are concerned, precursor complexes containing the number of metal atoms corresponding to the stoichiometry of the final oxide are required to optimize this approach, but this often represents an ambitious challenge. Otherwise, intimate mixtures of identical (or as similar as possible, with respect to the thermal behaviour) homometallic precursors of different metals to be combined can be used ('multiple precursors method').

Depending on the functionality of the polyaminocarboxylic acid and the total number of possible N and O coordination sites, various geometrical arrangements and coordination numbers can be achieved to fit the size and geometry requirements of the cations involved. In some specific cases, slightly modified ligands constitute promising alternatives. This is the case, for example, with the elements of groups IVB (Ti) and VB (V, Nb, Ta), for which well-defined soluble precursors exist. Peroxo-carboxylates [64–67] and peroxo-polyaminocarboxylates [68–70] of these metals are potential precursors, because they are available as water-soluble molecular precursors. However, due to the presence of the peroxo groups potentially triggering very exothermic decomposition, care has, however, to be exercised when handling these compounds at a large scale.

### Crystalline complex salts

Oxalates [71], tartrates [72] and citrates [73] of various metals can form well crystallized complex salts, e.g. $Mg(NH_4)_4(Al_xCr_{1-x}(C_2O_4)_3)_2 \cdot nH_2O$, which on thermal decomposition at moderate temperatures can yield mixed oxides. Although these complex salts permit substitution in large concentration ranges, or even in all proportion in some cases, of elements of the same ionic volumes, their stoichiometry is still rather rigid. This imposes a serious limitation on the wide applicability of the method. This limitation is conspicuous when comparing the chemical formulas of crystallized citrates that were mentioned in [1], Table 7, p. 111, and [46], with the very flexible composition of compounds that will be described in the next section. This difference concerns the nature of the associated elements and the stoichiometry. Very few crystallized citrates contain elements of primary catalytic importance, and nearly none of them contains two elements presently of interest for catalysis. On the other hand, stoichiometry is determined in a rigid way by the crystallographic structure. Oxalato-complexes had been the object of detailed studies [71–73]. They correspond to the formula:

$$M^I_2(NH_4)_4[M^{III}(C_2O_4)_3]_2\ nH_2O$$

where $M^I$ and $M^{III}$ represent a single metal or sometimes a mixture of simple ions of identical valency, namely I or III, respectively. This flexibility in stoichiometry, however, is restricted to within, respectively, the group of valency I or that of valency III. The method was also adapted for complex ions like the vanadyl cations $VO^{2+}$.

Geus and co-workers [74, 75] have applied another method based on chemical complexes. This is the complex cyanide method to prepare both monocomponent (Fe or Co) and multicomponent Fischer–Tropsch catalysts. A large range of insoluble complex cyanides are known in which many metals can be combined, e.g. hexacyanoferrate(II) (also called ferrocyanide) and hexacyanoferrate(III) (also called ferricyanide) with nickel, cobalt, copper, or zinc ions. Bimetallic precursors associating Cu cyano complexes with ammine or ethylenediamine complexes of Zn(II) were also described as model precursors to Cu–Zn oxide catalysts [76]. Soluble complex ions of molybdenum(IV) ($[Mo(CN)_8]^{4-}$) that can produce insoluble complexes with metal cations are also known.

The inconvenience in using the crystalline complex salts is the absence, or strong limitation, of flexibility in composition. This makes difficult or impossible to obtain catalysts with the needed composition. In general, the problem is further complicated due to the possibility of non-homogenization or phase separation during the chain of dowstream unit operations involved in catalyst production.

The amorphous complex method, described next, provides an escape from most of these difficulties.

### Amorphous precursor: 'citrate' method: general

The principle of this method consists of preparing a stable amorphous or glassy precursor that, thanks to the amorphous structure, tolerates an enormously wide range of composition. The starting solution is a mixture of metallic salts and a hydroxyacid such as citric, malic, tartaric, lactic, or glycolic acid [10, 77–79]. The name 'citrate' attached to the method is widely used because citric acid is cheap and stable and the vast majority of preparations use it rather than other hydroxyacids. The metals are preferably in the form of nitrates or ammonium salts, which will not leave any residues on thermal decomposition. In addition, the use of the nitrate and ammonium ions promotes surface area and porosity, due to the large amount of gas that is evolved during the decomposition. Typical concentrations are 1 g equivalent organic acid per equivalent of total metal content. The solution is concentrated by rapid evaporation under vacuum, for instance in a Rotavapor, until its viscosity exceeds 500 cP at ambient temperature. A very stable syrup is obtained in this way. It can be dehydrated under vacuum at about 80°C to a rigid-foam (meringue) precursor, which is amorphous to X-rays, hygroscopic, and exhibits the color of the metallic ions present. The amorphous precursor appears to be some sort of a three-dimensional polymer in which the multifunctional organic acids are linked to two or more cations by covalent or hydrogen bonds. The thermal decomposition of the amorphous mass may proceed more or less continuously or in two distinct steps at 80–100°C and 250–400°C. Because of the danger of violent reactions, this decomposition step is to be carried out very carefully, taking all necessary precautions. The preparation of oxides containing metallic ions highly active in oxidation needs very stringent precautions and is generally not advisable. In particular, the possible detonation of copper and silver salts should be borne in mind. In these cases, the freshly formed metal particles could be powerful catalysts for some unexpected reactions, e.g. with ammonia. Also, secondary reactions can occur even at room temperature resulting in the formation of a small amount of lethal cyanogen gas.

The mechanisms of reactions occurring during preparation of mixed oxides by the citrate methods have been outlined in some detail [80]. In the dehydration under vacuum, extensive loss of nitrate ions (in the form of various nitrogen oxides and ammonium nitrate) occur together with the loss of water. Although easier in the presence of citric acid, the decomposition of nitrate does not involve extensive reaction with the latter below 100°C. The semi-decomposed precursor obtained around 140°C is essentially a dehydrated, amorphous, highly porous mixed citrate. The higher temperature decomposition stage, mainly between 225 and 400°C, consists of the burning of citric acid by oxygen. This is facilitated because of the presence of nitrate ions in the initial precursor. As indicated above, this stage is catalyzed by the presence of metals whose oxides are oxidation catalysts. Additional details can be found in [9] and [80], as well as [81–85]. Some carbon remains in the oxides, as in most other preparation methods. The use of ozone has been shown to diminish the carbon content.

Mixed oxides obtained by the above method are very lightmass powders of apparent density most often below 0.05 g $cm^{-3}$. They are amorphous to X-rays, free flowing, and consist of aggregates of particles of 20–100 nm. Upon further heating, these oxides crystallize into various well-defined structures depending on the nature and composition of the starting materials: solid solutions, spinels, perovskites, garnets [11].

Variants of the citrate method consist of simply adding citric acid or other hydroxymultifunction acids to solutions used for preparing catalysts by other methods (precipitation, impregnation, sol–gel, etc.). Although not leading to such excellent results as the original citrate method, the result of such a use of hydroxyacids permits substantial improvements. A modified citrate method (commonly called the 'Pechini method') has been proposed in which a polyalcohol is added to the initial solution [86]. The polyalcohol is supposed to promote the reticulation in the transformation of the starting solution to the rigid foam. The reticulation or polymer formation is due to the esterification reaction between citric acid and the poly-alcohol. This method has been used for the preparation of barium titanates doped by a large variety of ions, and can be easily applied for preparing catalysts.

The chemical complexation methods and particularly those using amorphous precursors, have found important and innovative applications for the preparation of a wide variety of catalysts and supports and of various perovskite-type catalysts and barium hexaaluminates, as required for high-temperature (>1200°C) applications such as catalytic combustion. It is worthwhile describing some applications. This is done in the next two subsections.

### Example: preparation of $CeO_2$–$ZrO_2$ solid solutions

Ceria-zirconia solid solutions are important in catalysis because of their thermal stability and ability to store oxygen or, at least, to increase oxygen mobility in complete oxidation catalysts [87, 88]. They were investigated in the whole range of composition. In addition, their high heat capacity constitutes a strong advantage for the use of new techniques like the one employing reverse-flow reactors [89]. Extensive studies had been conducted on the Ce–Zr–O system after 1995 [89–97]. Actually the range of stability for application corresponds to phase metastability in the phase diagram [98]. Hence the advantage is to start from very homogeneous precursors, in order to avoid the presence of large regions where composition would correspond to strong thermodynamical stability and correlatively particles of low surface areas due to rapid growth of nuclei. X-ray diffraction (XRD) can indicate the presence of two phases, possessing the tetragonal and the monoclinic structure, respectively. Concerning the samples prepared by the citrate method, the observation of the XRD lines of both phases does not show any broadening that could suggest heterogeneity of composition. Different techniques, using in particular the MSI-CERIUS software, indicated that both polymorphic phases were solid solutions, as opposed to mixtures of monometallic oxides [83]. In contrast the samples prepared by the sol–gel method exhibited asymmetric XRD lines, and even the presence of stoichiometric $Ce_{0.5}Zr_{0.5}O_2$ as previously found in other studies (see references cited in [83]). The results of a detailed study of these samples (by XPS, EDX, Electron Microscopy, and the observation of the modifications of the XRD diagrams as a function of temperature during calcination of the precursor), in addition to the technique already mentioned, are reported in [83].

### Example: citrate method for the preparation of unsupported and supported perovskite catalysts

Many solids possessing the perovskite structure present interesting properties for complete destruction of harmful organic molecules by complete oxidation to $H_2O$ and $CO_2$ [94, 99]. In general, perovskites have been prepared by calcining a solid mixture of constituent metal oxides or carbonates (the method used in the ceramic industry), or by evaporating an aqueous solution of constituent metal nitrates or acetates with subsequent calcination. The resulting oxides have relatively small surface areas. The guiding principle here is to attain as thorough a dispersion as possible, almost to a molecular level, of constituent components in the precursors prior to calcination. Once this is achieved, lower calcination temperatures can convert the precursors to solids of the required perovskite structure with larger surface areas. Among recent examples are the preparations of $La_{1-x}Ce_xMnO_3$ ($x \leq 0.4$) [100] and $La_{1-x}Ce_xMn_{1-y}Co_yO_z$ ($x \leq 0.3$, $y \leq 0.7$) [101] homogeneous solid solutions. Nitrate co-precipitation apparently failed to give homogeneous solid solutions [102]. A comparison of the specific surface areas obtained with different techniques in the case of the perovskite $LaCoO_3$ is published elsewhere [97].

Teraoka *et al.* [98, 99] have applied the amorphous citrate process to prepare unsupported (or ‘neat’) and supported perovskites of the type LaMn, LaCo, LaMnCu, LaCoFe, LaCaCo, LaCaMn, LaSrMn, LaSrCo, LaSrCoCu and LaSrCoFe. The use of the citrate method for preparing atomically homogeneous oxides on supports has been a very important extension of the citrate method over the years. Nitrates of constituent metals of the required perovskite were dissolved in water and mixed with an aqueous solution of citric acid (molar ratio of citric acid to total metals approximately 1/1). Water was evaporated from the mixed solution using a rotary evaporator at 60–70°C until a sol was obtained. The sol was further dehydrated at the same temperature under vacuum for 5 h. Stabilized alumina of composition $La_2O_3 \cdot 19Al_2O_3$ was used as the support for the perovskites.

One of the carriers mentioned in the previous sub-section ($Ce_{0.8}Zr_{0.2}O_2$) has been used for supporting up to 20 mass% $LaCoO_3$ or $La_{0.8}Ce_{0.2}CoO_3$ [100]. The sensitivity of the XRD technique does not allow so solid conclusions as those obtained for unsupported phases, because the supported phase represents only a relatively small fraction of the solid investigated. At a loading up to 15 mass%, no difference appears between impregnation by citrates and by nitrates. For a loading of 20 mass%, however, a segregation of cobalt oxide is more important in the case of impregnation by nitrates in comparison with the use of citrates. In neither cases are evidences of some reaction between the supported perovskite and the support or of other kinds of decomposition of the supported phase. The activity of the catalysts obtained from citrates showed a slight advantage over the other series, but the conclusion of a critical discussion was that this could not be related directly to the quality of the supported solid solution.

It is interesting to indicate that Teraoka *et al.* also prepared the perovskites mentioned in results described above using an acetate process, instead of the citrate process. The acetate process needed a higher calcination temperature of 850°C and consequently produced samples the surface areas of which were only 1/3 to 1/7 of those of samples from the citrate process. The higher-area perovskites from the citrate process possessed higher catalytic activity for methane oxidation. For the preparation of supported perovskite catalysts also, the citrate process was more effective than the acetate process. This was confirmed in a more recent study [100].

Many attempts have been made to modify the citrate method [101–109]. Most of them were combining the original technique with other approaches. This will be mentioned in the next section. As an example, the solid precursor was decomposed under nitrogen and subsequently 'annealed' in air [106], namely submitted to special oxidation, in addition to that normally occurring because of use of nitrates in the citrate process. This could perhaps lead to further investigation, because one could suppose that (*i*) the presence of residual carbon after the first step may hinder sintering, and (*ii*) the succession of steps might modify a segregation of phases if this had been the beneficial effect.

### Hybrid complexation methods

The shortcomings of many widestread preparation techniques led to the use of hybrid approaches. The idea was to use complexing agents for improving catalyst homogeneity [58, 97]. This has been applied to different preparation techniques. The success of the 'citrate' technique made that the addition of citric acid, other hydroxy-acids and complexing molecules was used very frequently. Many different mixtures have been proposed as precursors, with amounts of complexing agent varying from small quantities to stoichiometric excess. It should be noted, conversely, that so-called 'modified citrate methods', instead of starting exclusively from citrates, also use organometallic salts, sulfates, chlorides, etc. (see, for example the preparation of $TiO_2$ and $TiO_2$–$ZrO_2$ oxides, in [102, 103]).

The success of these hybrid methods is very much dependent on the details of the procedures used and may concern only a few characteristics of the catalysts. In some cases, the advantage of these hybrid approaches is to modify the amount of carbon residue that probably can contribute to inhibit sintering [107]. Sulfates leave residues and chlorides often do so as well. The residues can act as modifiers or doping agents. The consequence could be alterations of catalytic activity and selectivity.

## Possible future developments

This article could not cover all the aspects of catalyst preparation where the reactivity of solid plays a crucial role. Other lines were developed, or will be covered in [97].

When future developments are considered, two directions, in particular, seem promising for the synthesis of solid catalysts of perfect homogeneity at the sub-nanometer level.

Speculative approaches would be to use specific colloidal or molecular interactions for preparing precursors of flexible composition.

The simplest idea would be to flocculate colloids constituted of species M, N, P, etc., carrying opposite charges in order to obtain three dimensional $–M^+–N^-–M^+–P^-–M^+$ clusters. There are very few publications dealing with this possible method. Current ideas correspond to very complicated approaches, like the synthesis of organometallic molecules containing all the desired metals in the desired proportions, that would be calcined or transformed in other ways under very mild conditions to a solid solution or a compound containing these two or several elements.

Another approach could be derived from the sol–gel process. Supposing that a given starting alkoxide species contained several elements in the right proportion, the hydrolysis could give a product uniform in composition. The difference with the conventional sol–gel method would be to start from a single building 'block', namely a complex alkoxide containing two or several elements, instead of a mixture of monometallic 'bricks'. Conceptually, this last approach corresponds to the way zeolites are constructed. Zeolites of different compositions and structure can be made because the building blocks are different. In zeolite synthesis, colloidal and van der Waals forces attach building blocks to each other. Formally, chemical links would do the same as in the way they act, for example, in the citrate process.

Since the middle of the nineties, considerable advance has been made in concepts concerning colloidal processes, molecular recognition, molecular assembly, new polymers and, generally speaking, processes allowing specific arrangements in space of chemical entities and chemical functions [106]. It can be noticed that molecular assembly may be assisted by solvents playing the role of templates [110]. Templates are also essential in assembling correctly the building blocks in zeolites. This analogy leads to new ideas for obtaining precursors of very flexible composition.

The problem in sol–gel process is the lack of selectivity in the formation of bonds between different alkoxides. This leads to an idea advanced by some specialists in this field, namely to attach different functions to the parts containing the different elements to associate. These functions could be selected in such a way that each of them only reacts with a single matching kind of function [1, 97]. A sort of elaborate 'Lego' structure can potentially be constructed according to this principle. An embodiment of such ideas for making various materials, including possibly surface-active structures, can be found in [106].

The two approaches described above for modifying the sol–gel process are quite distinct [97]. In one of them, a single alkoxide containing two or several different elements is used. In the other one, several monometallic species, each possessing two or several chemical functions, would have to be synthezised. These chemical functions should react selectively to another type of chemical functions, by a sort of key and lock recognition. Flexibility in composition of the product implies that at least three types of functions, and preferably more, be used. The challenges for chemical synthesis would be different, organometallic synthesis in the first case, functionalization in the second. These approaches will certainly show limitations, both for synthesis and flexibility of composition, that the citrate method does not encounter.

Another type of approach makes use of multifunctional polymers. This involves polymer-metal complexes based on structurally simple organic polymers such as poly(ethylene glycol), poly(vinyl alcohol), poly(acrylic acid), polyamide or polyimide derivatives. This permitted the synthesis of many oxide-type inorganic materials [108, 109]. Recently, investigations were undertaken for using more elaborate polymer structures: they consisted in polyampholytes resulting from the association of monomers bearing carboxylic acid and amine moieties. The objective was to synthesize polymer-metal complexes, which were converted into solid materials upon appropriate thermal treatment. Depending on the substituents present on the main chain, these polymers offer the advantage of tunable properties such as (*i*) solubility in various polar media, (*ii*) the number and nature of functional groups of each type, (*iii*) the presence of selected substituents able to induce controlled steric hindrance, (*iv*) cation complexation, or (*v*) formation of superstructures. This approach has been validated for the obtention of several transition metal molybdates, starting from inorganic precursors and a copolymer matrix made of diallylammonium and (functionalized) maleic or maleamic acid units [66, 111]. After removal of the solvent, homogeneous hybrid materials containing up to equimolar amounts of metals with respect to the 'repeat unit' of the copolymer can be obtained. An appropriate thermal treatment under oxidizing conditions generates the final oxide powder with very low residual amounts of carbonaceous species.

## Conclusions

In conclusion, making catalysts containing several elements homogeneously distributed in the solid at the sub-nanometer scale remains a major challenge and deserves more research than presently. Considered independently, neither solid state chemistry nor synthetic chemistry approaches alone, even assisted by chemical engineering, are able to provide simple solutions [58]. Breakthroughs may reasonably be expected from a cooperative work between several fields of scientific activity. Even when imperfect for lack of real molecular dispersion, the search for homogeneity could be a valuable objective, because phase cooperation now comes to the forefront of concepts in catalysis, in particular in oxidation reactions. Most methods used with the objective of ultimate atomic dispersion could turn out to be superior to other approaches if phase cooperation is the real objective, because they actually achieve a very fine inter-dispersion of zones with different properties. They could therefore give, together with other methods, more active and/or selective catalysts because contacts between phases would be more numerous.

In this chapter, the main topic has been the use of solid-state transformations to prevent segregation or large fluctuations of composition during the transformation of solid precursors to final oxide catalysts. On the whole, crystalline precursors do not permit the desired composition to be achieved, but they can be excellent for some specific cases. Amorphous precursors, especially those using polyfunctional hydroxy acids, can be prepared with almost any possible composition and can give the corresponding oxides. The initial aim of the method was to prepare solid solutions or oxides of two or several elements in well-defined structures, sometimes containing elements substituted within the normal lattice structure. A single other method has been claimed to offer similar flexibility. This is the sol–gel method. The two methods have still to be compared in detail. However, the kinetics of hydrolysis change very much from one alkoxide to another, with the consequence that the different elements sequentially get incorporated during gel formation. Regions, several nanometers in size, with different properties are formed.

When the objective is to prepare an extremely intimate mixture of two or more different oxides, each of them constituted of very small grains or particles, techniques such as spray calcination, oil drop, or freeze-drying, the complexation methods and the sol–gel method seem to have some valuable potential in principle. The use of a particular technique is then dictated by other considerations, such as the availability, stability and cost of starting material (especially for alkoxides) or ease of decomposition.

A very important remark should be added. The successful transformation of the precursors to a homogeneous oxide or a finely interdispersed mixture of oxides demands that diffusion leading to segregation be made as difficult as possible. In particular, the formation of liquid phases during decomposition and calcination of the precursor should be completely avoided. Unfortunately surface contamination is difficult to avoid.

Heterogeneous catalysts are not just chemicals in the ordinary sense of the word: they are performance chemicals or surface-active materials. Naturally, the performance of the catalyst will depend not so much on the initial composition or surface of the starting material, as on the real surface, as it is formed and stabilized and then changes dynamically under the prevailing process conditions. All the rules concerning the reactivity of solids [112] apply to the corresponding transformations. When designing and making reliable catalysts, it is necessary to take into account process parameters such as temperature, pressure, reactant concentration, and space velocity, as well as variable factors such as feed composition, and unpredictable or unsuspected factors such as impurities and poisons in the feed [113, 114].

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