

Introduction

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Chapter 1

Introduction

Abstract

Chemistry of materials gathers a wide range of chemical routes that allow producing materials for different processes. Researchers working on chemical synthesis constantly explore new material formulations with tailored properties and functionalities to run chemical processes at relatively low environmental costs and/or at high efficiency. Many impressive advances have been made in the chemistry of materials, from each of the major material classes, with a remarkable impact on novel and emerging technologies in the chemical industry.

In this scenario, the synergy between chemists and chemical engineers can boost the modernization of chemical industry although many challenges still need to be addressed.

Materials such as catalysts are regarded as the key parameter of a chemical process and their efficiencies do not only depend on the nature of the active phase but also on numerous features such as porosity (size, homogeneity, interconnectivity) and morphology, which are strongly dependent to the designed synthesis strategy. Moreover, most of the materials produced at lab scale in the form of micron-sized powders need to be extruded or wash-coated to be used industrially. These processes require binders and additives, whose interaction with the active phase can modify material properties

A comprehensive characterization of the prepared materials for a greater understanding of the complex relationships between specific modifications and the surface and bulk properties cannot be ignored. For this reason, development of modern tools to evaluate the materials structure and assembly processes are of utmost importance.

Besides the conventional methods (ion-exchange, impregnation, coprecipitation and hydrothermal method), advanced preparation techniques such as those relying upon the sol-gel chemistry can lead to smart materials with control of particle and/or pore size and/or shape at molecular scale.

Keywords: oxides, nanocatalysts, impregnation (co)precipitation, sol-gel method

1.1 The multifaceted role of oxides in heterogeneous catalysis

Metal oxides and mixed metal oxides are of tremendous current interest to scientists and engineers because of their potential applications in most industrial chemical processes [1]. These materials are known to possess some unique characteristics among inorganic materials such as high stability, in some cases, biocompatibility, cost-effectiveness, distinctive acid–base and redox properties. In addition, some metal oxides show exceptional ability to generate charge carriers under light irradiation resulting in improved electrical and optical characteristics.

In the field of heterogeneous catalysis, they are used either as catalysts or support for active species characterized by decisive physico-chemical properties and covering the largest family of catalysts. The main catalytic domains cover oxidation (selective or total), acid and base catalyses, hydrogenation, hydrotreating, photocatalysis, depollution and biomass conversion [2, 3].

Research in the field of metal oxides is always abuzz, both in academia and in industry, with the definition of novel catalytic formulations for targeted applications. Moreover, the ever-growing need for a green chemistry approach calls for new sustainable and reliable catalysts and processes.

Silica, Al₂O₃, TiO₂, ZnO, CeO₂, ZrO₂, porous and mesoporous metal oxides, multicomponent mixed oxides, polyoxometallates (POMs), the perovskites, and more recently the high entropy oxides (HEO) are some examples of heterogeneous catalysts, whether bulk or support, which play a decisive role in industrial chemistry [4-11].

The entry of nanotechnology into materials synthesis has further boosted the development of catalysts with enhanced properties with respect to the bulk counterparts. In this scenario, the bottom up synthetic strategies can help in the design of engineered materials replacing the trial and error approach. Considering structure sensitive reactions, besides the definition of the most suitable chemical composition, the research

has devoted much effort in tailoring the size and shape of solid particles, favouring morphology with specific crystal facet. The intent is always to increase the number of active sites and to control the nature of the exposed sites since the conversion of the reactants into the product occurs on sets of surface atoms.

A "creative disturbance" is a fascinating way to improve the activity of a metal oxide surface. This concept refers to the possibility of improving the catalytic activity of an oxide by replacing a small fraction of the cations of a "host oxide" with a different cation. An alternative way comes through the deposition of small MeOx clusters on the surface of another oxide (or any other insulator) [10].

Viewed from the perspectives of achieving designed properties and functionalities, the sol-gel method can be considered a powerful synthesis route possessing many advantages with respect to the conventional synthesis methods, such as the preparation of multicomponent materials with a one-pot process, the low temperature process, and high homogeneity. For this reason, by sol-gel synthesis a large number of sophisticated materials have been prepared whose properties are a function of the synthesis condition, Figure 1.1.

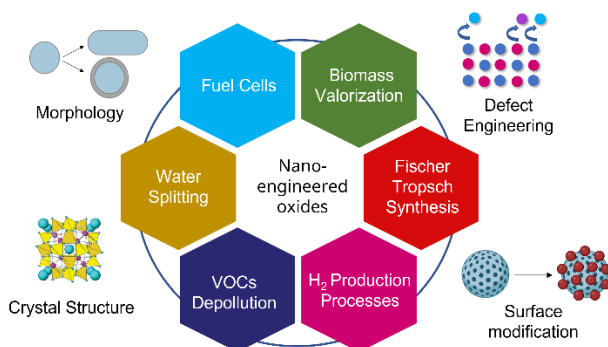


Figure 1.1 Nano-engineered oxides and application by sol-gel approach

1.2 Synthesis approaches to nanocatalysts

The progressive increase of the global population, the depletion of natural resources and the need to find alternative energy sources to fossil fuels related to the rising concerns over the emission of CO₂ have placed catalysis scientists towards new challenges in the context of climate change, pollution and sustainable energy [12]. In this scenario, many innovative strategies and approaches have been developed for the generation of renewable fuels, use of solar and wind energy, sustainable electricity generation and long-term safe and efficient energy storage [13-15]. In the materials science, more focus is currently being placed on manufacturing advanced catalytic formulations.

However, to support industrial processes in the direction of an effective ecological transition, helping to ensure the resilience of our society, the improvement of the catalyst performance is not enough. The design of reliable, sustainable and cost-effective synthesis protocols is also highly demanded.

A proper and systematic understanding of how effectively catalysts can be manipulated avoiding sophisticated synthesis route and harsh conditions can boost much more progress to scale up and meet practical production.

Nowadays, researchers focus most of the effort toward the synthesis of nano-scale catalysts with targeted properties for specific applications. Nonetheless, the effective utilization of nanocatalysts still involves many challenges, but the growing potential of nanotechnology sees more and more goals being achieved with the support of increasingly powerful materials characterization techniques [16].

Nanotechnology is concerned with the synthesis, characterization and application of materials and devices, changing their size and shape at the nanoscale. The concept of nanotechnology was first introduced by Nobel prize laureate Richard Feynman in 1954, whose famous statement is "There's a Plenty of Room at the Bottom". Since then, nanotechnology has quickly captured the attention of researchers who immediately realized the potential offered by this emerging technology. In fact, this field is constantly evolving to prepare materials with enhanced properties compared to their bulk counterpart. While nanotechnology is a powerful tool for governing and manipulating matter at the atomic level, nanoscience provides knowledge about the arrangement of atoms, molecules, clusters at the nanoscale [17].

The building blocks of nanotechnology are the “nanomaterials” whose properties depend on their size and shape. The definition of nanomaterial is still controversial but we can refer to nanomaterials when at least one of the dimensions is in the range 1-100 nm [18].

Different morphologies can be obtained depending on the number of dimensions on the nanoscale: nanoparticles, nanorods, nanosheets. Although nanomaterials are penetrating almost every field of science and technology, people are unknowingly using them in their daily lives. Compared to their large-scale counterpart, nanomaterials show distinct and sometimes unexpected properties mainly due to increased relative surface area and quantum effects. These factors can change or enhance properties such as the chemical reactivity, mechanical strength, thermal and electrical conductivity, antimicrobial activity, optical absorption. Since catalytic chemical reactions take place at the surface, the nano-structuring of catalysts ensures superior reactivity than bulk material. As a particle decreases in size, it exposes a greater proportion of atoms on the surface than on the inside. Therefore, nanoparticles provide more active sites and favourable surface features than larger particles [19]

The synthesis of nanomaterials can be viewed from two perspectives: on the one hand, the top-down approach in which typically mechanical methods (cutting, etching, grinding or ball milling techniques), electron beam lithography, atomic force manipulation, gas-phase condensation, aerosol spray, are used to cut and shape bulk materials. They are inherently simple with the possibility of large-scale production and no need for chemical purification. In addition to the limited versatility, the downsides are the imperfection of surface structure and the wide distribution of particle size and shape.

Alternative to the top-down method is the bottom-up approach, in which the nanomaterial is build up through assembling atoms, molecules and clusters.

This approach has many merits that make it attractive: fewer defects, a more homogenous chemical composition and better ordering. Furthermore, size, shape and surface properties can be engineered by selecting the building block and manipulating the process parameters.

Nano-architectures based on metal or metal oxide particles are the most widely used formulations in industrial processes. The common criteria for a high-performance catalyst are narrow size distribution and high dispersion on a selected support. In recent decades, the literature can count a proliferation of scientific works on the preparation of catalysts at nano-scale using a variety of synthesis methods. However, coprecipitation and impregnation are still the most used methods and probably the simplest approaches for the synthesis of different types of nano-catalysts. They often prove ineffective since they possess poor reproducibility and a scarce control of the particle size and shape, dispersion, crystallinity, and magnetic properties.

1.2.1 Impregnation method

The impregnation method, traditionally used for the synthesis of supported catalysts for a variety of heterogeneous reactions, involves loading a porous substrate with a metal precursor solution. The porous substrate can be prepared in a previous step if specific textural properties are desired, or it could be a commercial product.

The amount of precursor solution in relation to the pore volume of the substrate reveals whether it is wet impregnation (WI) or incipient wet impregnation (IWI). In both methods, the metal precursors are typically inorganic metal salts such as chlorides, nitrates and acetates. Although the type of metal precursor used in these syntheses is often the result of laboratory availability, the correct choice could have a crucial effect on the final dispersion as well as the drying and calcination temperatures [20].

The impregnation method implies the suspension of the catalytic support in an excess amount of a diluted aqueous solution of the metallic precursor. The most commonly used solvent for inorganic salts is water because of the high solubility of many precursors, whereas organic solvents are mainly used for organometallic precursors [21]. Uptake of the liquid into the pores of the support mainly involves diffusion phenomena. After an appropriate contact time, the mixture is filtered to recover the powder and leaving the liquid phase containing any precursor not retained by the support. This results in the need to recycle excess liquid to minimise precursor waste.

Impregnation is called incipient, or dry impregnation (DI), when the quantity of precursor solution is just enough to fill the pore volume of the substrate. In this case, the solution is drawn into the pores by capillary pressure. The lack of filtration step during DI synthesis of catalyst means that any counterions from the metal precursor salt, will be retained in the dried catalyst. When the solvent is water and the substrate an oxide, the liquid is considered wetting and will spontaneously penetrate the substrate. If the liquid is not wetting, external pressure is required to force the liquid into the pores [21].

To obtain the final catalysts with the zero-valent metal particles anchored onto the support, the impregnated and dried powder is subjected to thermal treatment in a reducing environment.

The catalysts obtained by WI method usually present higher metal dispersion and small clusters, which depending on the reaction, usually improves the catalytic activity.

1.2.2 (Co)precipitation method

The simplicity of the experimental set-up, the low cost, the absence of organic solvents and the high yield are some of the features that account for the widespread use of the precipitation method. It can be used to prepare either single component catalysts or supported and mixed catalysts [22,23].

In a typical co-precipitation reaction, hydroxides and/or insoluble carbonates are obtained by precipitation from an aqueous solution of metallic salts, usually nitrates, a chlorides or oxychlorides. The precipitation process can be induced by a change in conditions, such as temperature, pH value, solvent evaporation [24]. The filtered and washed co-precipitate is heat-treated at a specific temperature chosen according to the application. The most critical aspect concerns the degree of homogeneity of the system when precipitation involves more than one precursor salt. The weak point arises from the difficulty in managing the different precipitation rates and their pH dependence. From this point of view, the method shows low versatility. The precipitation rate is also crucial for controlling the particle size and distribution [25].

Co-precipitation is spotlighted as a simple, cost-effective and fast process for the synthesis of magnetic nanoparticles, such as pure iron oxides and ferrites in which iron oxides are chemically combined with one or more additional metals. Ferrites that can be represented by the formula MFe_2O_4 consist of a cubic crystalline structure of oxygen atoms with M (II) and Fe (III) in two different crystallographic positions.

Different ferrites can be obtained with high purity under oxygen-free atmosphere without requiring hazardous organic solvents, nor treatments under high pressure or temperature. Nevertheless, a few challenges still limit this method such as the control of the particle size and shape, crystallinity, and magnetic properties. Many authors have emphasised the importance of process parameters, in particular the type of alkaline agent, in controlling the chemical composition of nanoparticles and improving the magnetic response [26,27].

1.2.3 Hydrothermal/solvothermal process

The term hydrothermal is used when the synthesis is carried out in an aqueous solution in a sealed reactor, known as an autoclave, under autogenous pressure. The strengths of hydrothermal synthesis are the relatively mild operating conditions (reaction temperatures < 300 °C), the one-step synthesis procedure, environmental friendliness and production of fine crystals with high purity and controllable morphology.

The formation of the nanomaterial is the result of a sequence of nucleation and crystal growth processes [28]. The solubility of ions plays a critical role within the hydrothermal medium as its decrease leads the system to supersaturation conditions resulting in the precipitation of nanoparticles. This supersaturation acts, then, as the driving force of nucleation and growth.

The growth conditions of crystals determine their relative morphology and size. A mineralizing agent may be added to the solution as key factor to tailor the crystal size. In addition, process variables such as temperature, pH, reactant and additive concentrations are the tools to modulate the properties of the ceramic oxides produced under these conditions.

The crystal growth mechanisms under hydrothermal/solvothermal conditions is still debated, including identifying the growth unit attached to the surface of crystal entities and controlling steps in the crystal growth process.

When organic solvents replace water in the synthetic procedure, the process is called solvothermal. The chemical reaction proceeds at a temperature above normal boiling point of the solvent increasing the solvent's ability to dissolve solids. The solvothermal process can be very advantageous when handling precursors that are water-sensitive and also favours the use of relatively low temperatures and pressures [29].

Although this method has been greatly improved in recent decades, for example by coupling it with microwave technology, some major weaknesses remain, including the long reaction times, the discontinuity of the process and the inhomogeneity of the heating.

1.3 Sol-gel chemistry for oxides preparation

For the fabrication of increasingly efficient catalysts that strengthen established technologies but are also able to promote the development of new ones, it is necessary to direct research towards the rational design of materials with controlled nanoarchitectures to increase their performance in applications, rather than developing randomly shaped nanomaterials. In this scenario, sol-gel technology offers unparalleled potential for assembling atoms, molecules and small clusters into structures with controlled size, shape, crystallinity and tailored surface functionality, Figure 1.2.

The sol-gel techniques were firstly developed to prepare glasses and glass ceramics at low temperature, as alternative to conventional melt-quenching method [30, 31]. The sol-gel approach relies on the principles of organic synthesis and products are formed in kinetically controlled reactions from molecular precursors, whereas the thermodynamically favourable crystalline structure is avoided by fast enough cooling when glasses are formed from melts [32-33]. The sol-gel was defined as a "chimie douce" route as opposed to the less sophisticated ceramic methods [34]. However, dealing with a bottom up approach (for materials synthesis) implies the understanding and control of the process parameters to drive the assembly of molecules and clusters into an useful structure and that should be the guiding principle to reap the benefits of sol-gel method.

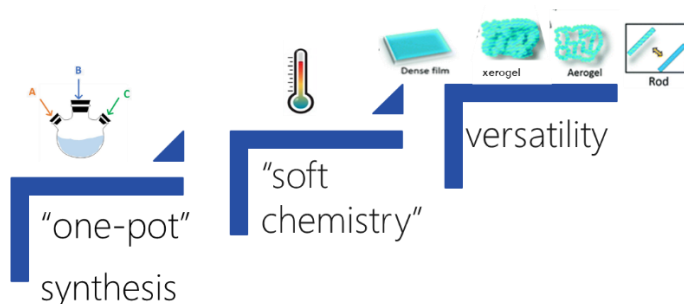


Figure 1.2 Representation of the main features of sol-gel synthesis

Although the sol-gel route can be described as the sum of two distinct phases, solution and gelation, depending on the adopted approach, the gelation process may change significantly. We have to distinguish between so-called "polymeric gels" (generally those gels derived from metal alkoxide syntheses) and "colloidal gels" (through controlled destabilization of the nanoparticle dispersion) [30]. In the case of colloidal gels, as in the case of silica particles obtained by the Stöber method, all the sol-gel processes can be described in the nanoscale [35-37].

The sol-gel chemistry offers some particular advantages, centred on the ability to produce a solid-state material ensuring mixing of reagents at atomic level. With this method, advanced inorganic materials such as ternary and quaternary oxides with controlled particles morphology and size can be obtained at low processing temperatures and short synthesis times. It is worth noting that producing a homogeneous

precursor at room temperature does not ensure homogeneity throughout a reaction and many sol–gel routes have therefore been designed to overcome the problem of possible segregation during synthesis.

The sol-gel chemistry met the challenge for the molecular engineering of nanomaterials making possible the chemical construction of materials with defined architectures. Indeed, the sol-gel technique can be seen as the most dynamic, reliable, and versatile bottom-up synthesis method that has received enormous interest in several research fields, extremely valuable for the preparation of oxide-based systems with enhanced properties.

The sol-gel chemistry overwhelmingly entered the heterogeneous catalysis with the synthesis of mesoporous silicas, in 1992 at Mobil oil company [38]. These medium- to long-range ordered porous structures allowed more facile diffusion of bulky molecules overcoming pore size constraints encountered in zeolites materials. [1-2]

Despite the great progress made in the preparation of the mesoporous silicas, a land of opportunities is offered by the self-assembly of organic surfactants acting as structure directing agents. Titania is the semiconductor par excellence in photocatalytic processes and the templating-assisted method resulted strategic to promote specific crystal phases and shapes with enhanced reactivity, making it competitive with the commercial Degussa P-25. [9, 39-40].

Compared to the most popular TiO₂ counterparts, catalysts based on CeO₂-NPs offer promising opportunities in name of better response in the visible region of the solar spectrum and long lifetime of charge separation [41]. Moreover, the greater affordability compared to Ti [42], makes CeO₂ a strong economic competitor. The pivotal role in catalysis arises from the low activation barrier for generating lattice O vacancies as consequence of the shuttle between Ce(III) and Ce(IV) [43]. Among the preparation methods, the sol-gel synthesis in a water-in-oil microemulsion is reported to be advantageous as it can ensure a narrow particle size distribution and the possibility to tune the physico-chemical properties controlling the amount and type of defects [44-45].

Semiconductors inorganic oxides are key ingredient in the formulation of many (photo)catalysts: ZnO, WO₃, and SnO₂ based catalysts represent highly prospective candidates for the degradation of recalcitrant pollutants in the name of their activity in many photo-oxidation processes [46-47]. The (sol-gel) Pechini method, whose chemistry goes back to that of metal complexes, is a valuable alternative to obtain remarkable homogeneity and purity in the preparation of mixed oxides [31, 48].

Within the big challenge to convert solar energy into electricity and/or chemical energy, photoelectrochemical (PEC) water-splitting is the new horizon for the production of green hydrogen as an ideal secondary energy source. Ongoing research is focused on improvements in efficiency, durability, and cost. In (photo)electrochemical processes where semiconductors are used as (photo)electrodes, the added value of sol-gel comes from the possibility of employing the homogeneous solution that was obtained before the gelation to prepare thin films by means of spin and dip coating.

A further advantage is the possibility to enhance the photocatalytic activity by modulating its ability to absorb light in the visible range through doping, creating defect states in the band gap or introducing energy levels in it [49-50]. Specific sol-gel routes can be designed to favour the effective inclusion of heteroatoms in large(r) amounts [9].

Thermal and chemical stability, excellent mechanical properties along with a low concentration of Lewis acid sites and/or the presence of basic sites are some of the distinctive properties of zirconia that keep it activities in many reactions, either as catalyst or support for active metal sites [51-52]. The central role of zirconia in catalysis is even more relevant if we consider the use of functionalized zirconia acid catalysts [53-54]. However, the inherent limitations of zirconia can be related to the sintering phenomena, extent of crystallite growth, and the extent and rate of phase transformation on calcination [55]. The skilful sol-gel chemistry can restrain the loss of surface area and the formation of a micropore structure promoting the formation of mesopores with appropriate synthesis strategies [53, 56].

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