

Evolution of Sol–Gel Chemistry

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Chapter 5

Evolution of the sol-gel chemistry

Abstract

Since the early studies on hydrolysis and condensation reactions of silicon alkoxides, progress in the knowledge of sol-gel chemistry and its potential has never stopped. The possibility of varying both parameters and precursors is boundless, resulting in ever more finely tailor-made materials. Furthermore, the continuous development of this technique has produced an impressive number of new syntheses and procedures that exploit different chemistries. A typical example of this is the development of organic-inorganic hybrid materials that combine the benefits of the organic matrix with the properties of the inorganic part, leading to new fields of application. The non-hydrolytic sol-gel is, on the other hand, an elegant and versatile method that allows remarkable levels of homogeneity to be achieved in the preparation of mixed oxides, as well as favouring the formation of defined polymorphs. Another particularly valuable route for the preparation of mixed oxides is the Pechini method, which overcomes most of the complexities and inconveniences that often occur in the alkoxide-based sol-gel process. In this chapter we retrace the main developments in the sol-gel method, reporting on the most interesting advances in the framework of catalytic application.

Keywords: organic-inorganic hybrids, Pechini method, non-hydrolytic sol-gel

5.1 Organic-inorganic hybrids

Hybrid materials can be defined as the nano-scale combination of two components, one (bio)organic and one inorganic. This class of material is not an ingenious human invention but rather one of the countless expressions of nature's magnificence. The physico-chemical properties are enhanced by the synergistic effect of the two components, giving rise to interesting and intriguing properties that have opened up promising horizons for a new generation of multifunctional materials [1,2].

A productive and multi-disciplinary field of research arose with a view to imitating nature in order to design and produce sophisticated and inexpensive materials that would respond to the industrial needs triggered by technological progress. The sol-gel method, offering extreme versatility in underlying chemistry and mild operation conditions, immediately emerged as a leading player in the development of tailor-made hybrid materials with well-defined architecture [3].

Hybrid materials, often biologically inspired, resulting from sol-gel synthesis strategies are countless. Their progressive and ever-increasing penetration in various industrial fields can also be attributed to the easiness of processing them into different shapes [1].

The distinctive properties of this class of materials are closely dependent on the nature of the interaction between the inorganic matrix and its organic counterpart. A rational design of advanced hybrid materials necessitates an understanding of the type of interface that can be generated in the coupling of the different components. This enables the best synthetic route to be outlined to enhance the right properties for applications in the fields of catalysis, sensor technology, optics and nanomedicine.

A distinction made on the type of interaction that can occur between the organic and inorganic fractions allows hybrids to be divided into two classes. Class I contains hybrid materials characterized by the absence of strong bonds between the organic and inorganic components. They rather interact through weak interactions: van der Waals forces, π - π interaction, hydrogen bonds or electrostatic interactions.

When, on the other hand, the two components are connected through covalent bonds, we obtain what are classified as class II hybrids [4].

The organic moiety can consist of monomers, oligomers or polymers and may contain any functionality. The organic block can also be represented by a biologically active molecule, such as an enzyme. The inorganic species are molecular systems able to form inorganic networks and can also contain organic functionalities. Actually, a large number of hybrid architecture can be designed and Figure 5.1 reports two examples of class I hybrid materials [5]. TEOS can be mixed with an organic phase (e.g. poly(vinylpyrrolidone)) allowing SiO_2

network to be formed within the organic phase. In this case, the organic polymer and the silica network are held by hydrogen bonds formed between hydroxyl groups of silica and the carbonyl groups in polymer chains, Figure 5.1A. Another approach that leads to a type I hybrid can be the simultaneous gelation of the inorganic and organic components that form an entangled independent network of an organic polymeric gel and a silica gel like, Figure 5.1B.

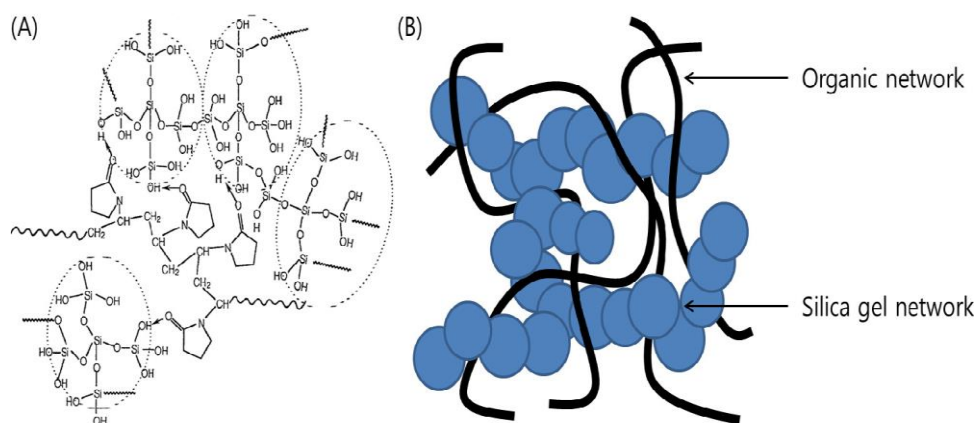


Figure 5.1 Schematic representation of (A) molecular structure of PVP-silica hybrid and (B) hybrid with interpenetrating SiO_2 and organic gel networks structure [5]

Although these hybrid materials featured appealing properties for heterogeneous catalysis, some downsides limited their use. Easy separation of products and the possibility of catalyst reuse are some of the main advantages of heterogeneous catalysis. As fully explained by Diaz et al [6], the use of class I hybrid catalysts, in which the organic phase is generally trapped in the pores of the inorganic network, exhibit leaching, deactivation and desorption problems of the active organic moiety.

The need for a more robust hybrid matrix that preserves the integration of the two fragments has driven catalytic research toward synthetic strategies for the preparation of class II hybrid catalysts. The challenge is to have the organic fraction uniformly distributed over the entire catalyst without being confined within the walls of the solid by limiting its porosity [6].

Some type of fascinating architecture within the class II hybrid materials are mentioned in the book of Alain C. Pierre [7].

A possible arrangement arises from the presence of chains with alternating organic and inorganic moieties; in this subclass, neither of the two components can participate in an independent 3D network and the precursors must contain groups that allow copolymerisation. The two components do not necessarily have to be linear, but can also consist of rather dense nanoparticles or clusters. Additionally, it is possible to have core-shell structures in which the organic phase covers the colloidal silica particles.

The use of alkoxides modified with organic groups can be extremely effective in the preparation of Class II hybrid catalysts. The hydrolysis and condensation of an organically modified precursors leads to the formation organically modified sol-gel materials, known as Ormosils (organically modified silicates), whereas Ormocers (organically modified ceramics) are obtained when an alkoxide of a metal other than silicon is used [8]. The physical and chemical properties of ormosils can be easily tailored by modulating the amount of modified precursor or changing the type of functional group. The introduction of various organic functional groups can either be an attachment site for subsequent covalent anchoring of active organic groups or serve for copolymerisation with organic monomers. The utilisation of an organically modified precursor was also proposed to tune the gelification kinetics and better control the shaping process. A further advantageous feature of hybrids is the possibility of juggling with the hydrophobic character through the introduction of specific organic groups. Organic-inorganic precursors can be monomeric species, $\text{R}'\text{Si}(\text{OR})_3$, bridged $((\text{R}'\text{O})_2\text{SiR}'\text{Si}(\text{OR}')_2)$ or polyhedral oligomeric (POSS) silsesquioxanes [6].

The flexibility of chemistry relating to the preparation of silicon alkoxides provides a very large number of organically modified alkoxides where the functionalities introduced can be of any nature (alkyl, aryl, acrylic, epoxy. . .). The 3-(methacryloyloxy)propyl trimethoxysilane, Figure 5.2a contains both hydrolysable alkoxide groups and organic groups susceptible to polymerization so it can lead itself to a hybrid material of class II. Hybrids can also be obtained by the simultaneous polymerization of alkoxide or alkyl alkoxides and polymer monomers like 2-hydroxyethyl methacrylate, Figure 5.2b. Regardless, synthesis strategies should always be designed for obtaining hybrid networks at molecular level, bridging the inorganic and organic structures. Indeed, the introduction of one or more organic groups leads to different reactivity with respect to TEOS because the steric and electronic properties of the R' group on the silicon atom strongly impact on the nucleophilic substitution.

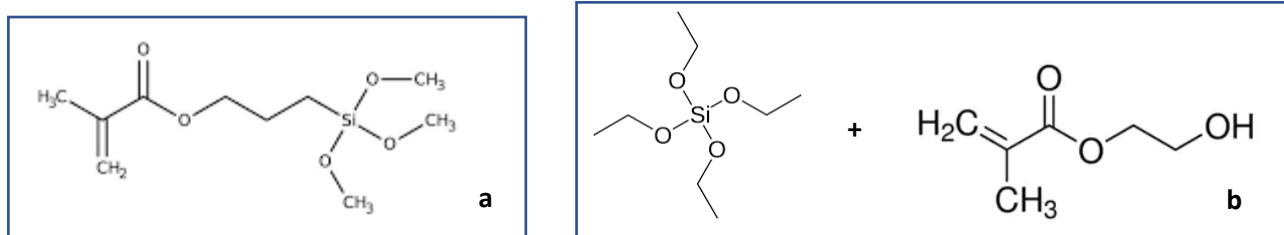


Figure 5.2 (a) Precursor of an hybrid material of class II: 3-(methacryloyloxy)propyl trimethoxysilane; b) Si alkoxide and 2-hydroxyethyl methacrylate

A valuable and significant contribution to the development of hybrid catalytic formulations with advanced properties over single-functional solids or homogeneous catalysts was conducted by Katz et al., Davis et al. and Corma et al. [9-12]. Working mainly on amorphous silica, they evaluated the cooperative effect of several different active groups obtaining multifunctional and versatile heterogeneous catalysts.

We conclude this section with a quick mention of the possibility of obtaining biocatalysts by using biological molecules such as enzymes as organic fraction. Enzymes are well known as highly effective and efficient catalysts of a wide variety of processes characterised by high selectivity and activity. To improve the stability of the biomolecules under various reaction conditions and to enhance the reusability of biomolecules over successive catalytic cycles, enzyme immobilisation is the widely used technique. The material chosen to support the enzyme must meet very strict criteria and from this point of view the flexibility of the sol-gel method makes it a powerful platform through which it is possible to tailor the porous structure, surface area, hydrophobicity, biocompatibility, surface properties, surface functionalization [13,14].

5.2 Non-hydrolytic routes

The Non-Hydrolytic Sol-Gel, NHSG, is a fascinating and alternative bottom-up route to overcome certain limitations of the classical alkoxide-based sol-gel method. The name "non-hydrolytic" refers to the drastic change of the reaction medium as the processes take place in a water-free environment.

This method can be particularly beneficial for the preparation of mixed oxide catalysts or hybrid systems with strictly controlled morphologies, crystallinity and porosity [15,16].

In the preparation of mixed oxides, where alkoxide precursors are typically used, a first obstacle encountered is the difference in reaction rates. The production of a homogeneous gel from hetero-condensation reactions is pursued using a some "gimmicks". A relatively straightforward approach involves acid prehydrolysis of low reactive alkoxides, such as silicon precursors, and chemical modification of the metal alkoxides. However, controlling the reaction pathway remains challenging making the material hardly tailorable. Moreover, the addition of certain additives can make starting materials more costly and less environmentally friendly.

The presence of water can also be a drawback in view of the miscibility of precursors and hydration phenomena affecting the reactivity of species and the surface energy of clusters. Non-Hydrolytic Sol-Gel can be seen as a way to ensure a better homogeneity in the case of mixed oxides.

To properly define a synthesis pathway as non-hydrolytic, it is necessary to completely rule out the presence of water, including as a product of polycondensation reactions [16,17].

As represented in Scheme 5.1, the chemistry of NHSG relies on a sort of condensation where the formation of the M-O-M bond is ensured by an oxygen donor other than water.

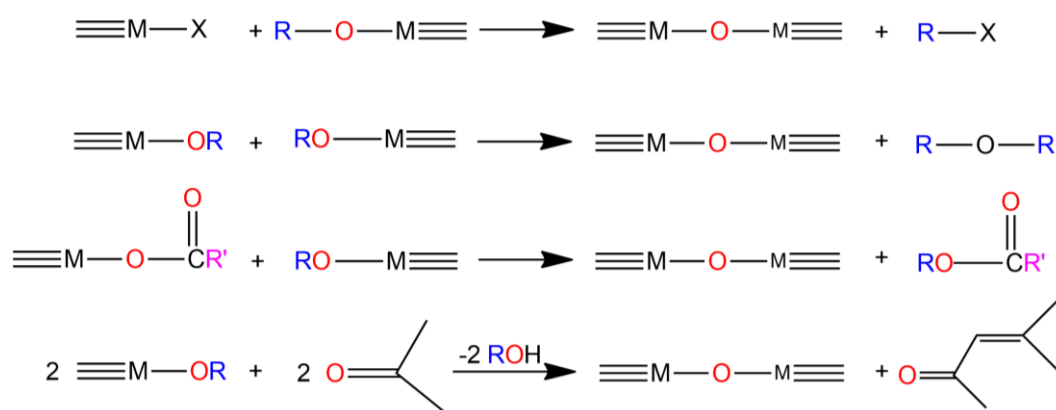
Typically, organic substances (e.g. alcohols, carboxylates or the alkoxides themselves) are used as oxygen donors. The reactions are generally much slower than those in an aqueous environment providing improved control over the composition, structure, and texture of the resulting materials. Indeed, the performance of heterogeneous catalysts is often strictly correlated to the presence of specific polymorphs as well as a well-defined morphology. A noteworthy example is titania, a material featuring unique properties that trigger its cross-cutting presence in catalytic processes of industrial interest. The non-hydrolytic sol-gel enables some of titania's main characteristics to be modulated by playing with synthesis parameters, such as the nature and type of oxygen donor, solvent or temperature, avoiding elaborate synthetic procedures [18,19].

Another important feature that should not be ignored in catalyst design is the type of porosity and relative pore size distribution. Conventional methods, with particular reference to polymer networks, generally produce poorly cross-linked monolithic gels that under unfavourable capillary forces collapse into microporous structures. For this reason, templates or drying systems under supercritical conditions are often used. Although NHSG also requires a solvent removal step, a greater extent of condensation capable of withstanding capillary stresses and lower surface tension of organic solvents compared to water yield mesoporous xerogels sometimes featuring distinctive textural properties. Further tailoring of the porosity toward an ordered mesoporosity can be achieved with the addition of a structure-directing agent [15].

The water-free reaction medium has also a remarkable impact on the surface chemical properties. Unlike oxides obtained by the conventional method that are rich in hydroxyl groups, the surfaces of nanoparticles obtained by the nonhydrolytic method expose organic groups that may belong to the precursors, the oxygen donor, or the solvent. In addition to the hydrophobic character they impart to the particles, these organic groups can promote the formation of nanoscale crystallites and possibly be used for subsequent surface functionalization.

In conclusion, non-hydrolytic sol-gel can be seen as a versatile one-pot procedure that relies on organic reactions while providing ample leeway to address specific requirements concerning the composition, texture, structure, and morphology of the final material.

NHSG is a particularly well-established and powerful methodology for the synthesis of mixed oxide catalysts, where adjustable porosity, homogeneous dispersion of metal cations and active surfaces are particularly sought-after features [16].



Scheme 5.1. M-O-M bonds formation by nonaqueous sol-gel approaches

5.3 The Pechini method

When Maggio Paul Pechini worked for the Sprague Electric Company in Massachusetts in the 1960s, ceramic capacitors were prepared by a conventional solid-state reaction method. The limitations associated to the latter, such as the non-homogeneity of the final product, long milling times, high temperature, and the

presence of contaminants, prompted Pechini to investigate an alternative preparation process [20]. The method named after him was developed for the preparation of lead and alkaline-earth titanates and niobates and patented in 1967 [21].

The Pechini method is a wet chemical method that can be considered a modification of the sol-gel method. This procedure is particularly helpful when alkoxides cannot be used because they are expensive, too reactive or simply unavailable. Since its original definition, the 'Pechini process' has continuously evolved towards the synthesis of many metal oxides in bulk shape, as nanocrystalline powders and in thin films, and it is currently applied all over the world at the industrial level.

The chemical reactions behind the Pechini approach, and which replace those of hydrolysis and condensation of alkoxides, are mainly complexation and esterification [22]. As illustrated in Figure 5.3, a complex is generated between the metal cation and a hydroxycarboxylic acid. The polybasic carboxylic acid chelates are then cross-linked with the addition of polyalcohols that bind to the carboxyl groups via esterification reactions.

The demand for less organic matter, more nature-friendly compounds for a more sustainable process, and an extension of the method to a large number of metals drove research towards a modification of the method by introducing water as the main solvent medium and replacing citric acid and ethylene glycol with other carboxylic acids and polyols, respectively. In a typical preparation, metal salts (typically nitrates, chlorides, acetates) are dissolved in water in the presence of a tricarboxylic acid and a polyalcohol. The mixture is then heated to remove the water and obtain the polymer-like resin. Finally, the elimination of organic compounds is promoted by the subsequent heat treatment at around 400 °C [23]. The feasibility, versatility, and relatively low cost together with the high degree of purity and homogeneity achievable in the preparation of mixed oxide systems makes the method very attractive. Nevertheless, some weaknesses of the method in synthesis design must be considered. Careful pH control is imperative to avoid precipitation of individual hydroxides that would deviate the composition of the final product from its nominal composition. It is generally optimized using ammonia, ammonium hydroxide or other bases. pH is also a pivotal factor in determining the stability of the complex. From this point of view, for some metals, such as alkaline earth metals, the stability of the chelated complex may require the use of additional complexing agents, like EDTA (Ethylenediaminetetraacetic acid).

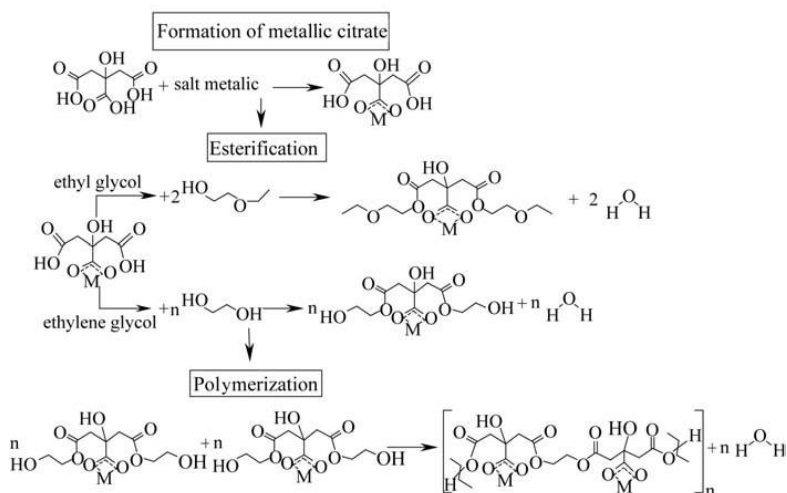


Figure 5.3 Pivotal reactions of the Pechini process. h. Adapted with permission from [22]; Copyright 2004 Springer.

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