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*Journal of Materials Chemistry – Theme Issue on Green Materials*

Feature Article

## **Introducing ecodesign in silica sol-gel materials**

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Niki Baccile was born in 1978 in Italy and discovered the intriguing world of material science with the Japanese cartoon series *Hurricane Polimar*. To fulfil his dreams of inventing the self-healing red dress, he studied Material Science at the University of Padova, where he obtained his *Laurea* (master degree) in 2002. Instead of working on self-healing polymers and tissues, he joined the Laboratoire de Chimie de la Matière Condensée de Paris (LCMCP, Paris, France) under the supervision of Dr. Clément Sanchez and Florence Babonneau. In 2006, he obtained his PhD degree on the synthesis and solid state NMR characterization of mesostructured silica materials. During his two post-docs at the Charles Gerhardt Institute (Montpellier, France) and Max Planck Institute for Colloids and Interfaces (Potsdam, Germany), he combines materials synthesis and green chemistry approaches. These topics became his research priorities since late 2008, when he joined LCMCP as a permanent CNRS researcher.

Florence Babonneau, born in 1957, is Directrice de Recherche at CNRS since 1995. She is currently leading the “Sol-Gel Materials and NMR” group in the Laboratoire de Chimie de la Matière Condensée de Paris (UPMC-Paris6). Her main research interest is centred on detailed structural characterization of a variety of chemically-derived materials, using mainly, but not exclusively, high resolution solid-state NMR. She is currently interested in silica-based organic-inorganic materials and calcium phosphate biomaterials focussing on the description of organic-inorganic interfaces.

Bejoy Thomas studied chemistry at the University of Bangalore (India) and received his Ph.D. in physical chemistry from Cochin University of Science and Technology (India). After working for some time in NMR spectroscopy at Indian Institute of Science (India), he moved to Germany as a DFG postdoctoral fellow at Institute of Chemical Technology, University of Stuttgart. The focus of his work is synthesis of hierarchical zeolites, ordered mesoporous materials, surface science, and catalysis, and *in situ* NMR spectroscopy of working catalysts. He is currently a postdoctoral associate at the Laboratoire de Chimie de la Matière Condensée de Paris, UPMC-P6.

Thibaud Coradin, born in 1970, is Directeur de Recherche at the CNRS since 2007. He is currently leading the « Materials and Biology » group in the Laboratoire de Chimie de la Matière Condensée de Paris (UPMC-P6). His research topics include silica biomineralization, green sol-gel chemistry, bionanocomposites, biomaterials and sol-gel bioencapsulation. He co-authored over 75 publications and 10 book chapters. He is a member of the Advisory Editorial Board of *Current Medicinal Chemistry* and *Silicon*.

## **Abstract**

Over the last decade, ecodesign has been introduced as a concept and a methodological framework to identify and improve sustainability in product development. In this context, the 12 principles of Green Chemistry provide suitable guidelines for the elaboration of molecules and materials in conditions that meet some ecodesign-related criteria. Sol-gel chemistry is an interesting domain to be examined in this perspective because it was early identified as an eco-friendly process compared to the traditional routes to ceramics and glasses. Thus it is not surprising that many recent developments in sol-gel technology have, explicitly or not, addressed sustainability issues. In this review, we present an overview of these advances, focusing on the chemistry of silica. Starting from the typical reaction involving tetraethoxysilane hydrolysis and condensation in hydro-alcoholic media in the presence of inorganic catalysts, the current alternatives in term of precursors, solvents, catalysts and activation sources are presented. As an example of hybrid materials, the synthesis of surfactant-based mesostructured silica is commented. Manufacturing methods to nanoproducs, including sol-gel technology are also discussed in terms of sustainability. Finally, the recyclability and degradation of sol-gel silica are shortly commented. As a conclusion, some perspectives and current limitations for the development of a “greener” sol-gel chemistry are provided, extending the discussion to non-silica materials.

## 1. Introduction

Life Cycle Engineering (LCE) can be defined as “the application of technological and scientific principles to the design and manufacture of products, with the goal of protecting the environment and resources, while encouraging economic progress, keeping in mind the need for sustainability, and at the same time optimizing the product life cycle and minimizing pollution and waste”.<sup>1</sup> The idea of sustainability introduced by LCE is very broad and it touches too many domains like minimization of pollution/waste, economic progress, green design, environmental protection, social concern, ecodesign and many others. Generally speaking, LCE contains the necessary theoretical information to create a product at the lowest environmental cost. LCE encloses the concept of Life Cycle Assessment (LCA) which is more focused on the evaluation of the entire life cycle of a given product, and it can be defined, among other ways, as “an objective process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and material usage and environmental releases, to assess the impact of those specific energy and material uses and releases on the environment, and to evaluate and implement opportunities to effect environmental improvements.”<sup>1</sup> In simple words, LCA provides the tools and methodology to assess the impact of a specific product and to quantify such an impact. In the end, LCA defines the boundaries for the conception of an environmentally-benign product and it constitutes the starting framework for the concept of ecodesign. Ecodesign focuses more on the integration of environmental considerations in product development and was proposed as a new approach in product conception by the United Nations Environmental Program (UNEP) in 1997. Ecodesign defines “sustainable solutions to products, services, hybrids or systems that minimize negative and maximize positive sustainability impacts – economic, environmental, social and ethical – throughout and beyond the life-cycle of existing products or solutions, while fulfilling acceptable societal demands/needs.”<sup>2</sup>

Ecodesign is thus more concerned with conceiving ecological and economical tools for those designers involved in the making of the product.

Four levels of ecodesign can be identified: 1) product improvement; 2) product design; 3) new product concept definition; 4) new product system definition.<sup>3</sup> Impact studies and certification can be used to direct the conception of the final product according to the points above. After pointing out the weak non-sustainable points, progressive improvement and re-styling occur throughout the product conception. If needed, the product can actually be re-designed and, in case the effort would not meet the best “eco”criteria, a completely new product, or even a production system, could be imagined. In order to avoid time waste, a number of guidelines, suggestions, checklists and analytical tools exist in the literature. Often, the starting points are the so-called white, gray and black lists classifying products from the lowest to the highest impact, with the black list contains all those materials whose use is actually forbidden. These lists suggest some general simple rules such as: 1) avoid toxic substances; 2) minimize energy, transport, and resource consumption; 3) promote long-life; 4) invest in better materials to protect from dirt, wear and corrosion; 5) organize an upgrading and possibility of repairing and recycling.<sup>4</sup>

Finally, a number of indicators and analytical tools have been developed in order to quantify the impact of a product. One very simple concept is the estimation of a product’s *eco-efficiency* and calculation of the so-called *Factor X*. *Eco-efficiency* is a simple ratio between the product (or service) value and the environmental influence, while the *Factor X* is the ratio between the *eco-efficiency* of the evaluated product (or service) and the *eco-efficiency* of the reference product (or service).<sup>5</sup> All data involved in the production (energy consumption, quantity of matter, transport, recycling, social cost, and so on) of the object are estimated and indicative values quantifying *eco-efficiency* and *Factor X* can be determined. Aoe proposed a visual way to relate *Factor X*, *eco-efficiency* and their implication in the

overall design (Fig. 1).<sup>5</sup> The chart connects the functional performance of a product with respect to its environmental impact. Whenever the *Factor X* degrades below one, the impact is considered as being high. On the contrary, whenever the *Factor X* is higher than one, the product falls in the domain of ecodesign. How much is “eco”? Ideally, the A region is what ecodesign aims at while regions B and C have the downfall of either low functionality or high impact.

More sophisticated tools have been developed over the past 15 years. Among them, the Environmental Design of Industrial Products (EDIP) was developed in 1996, the CML and CML 2 (from the Center of Environmental Science of Leiden University in the Netherlands) were developed in 1992 (CML) and updated in 2000 (CML 2), the Eco-indicator’95 (EI’95) and Eco-indicator’99 (EI’99) were developed under the Dutch NOH programme, the Environmental Priority System (EPS) exists since 1993.<sup>6</sup> All indicators try to establish the necessary standards to compare data of different origins and they identify in a more or less precise way the categories on which the impact has to be measured (global warming, ozone layer depletion, human toxicity, ecotoxicity, acidification, carcinogens, solid waste, radiation, etc...) and attribute a weighting hierarchy to each of them.

Most studies on the application of ecodesign have been done on electronic goods (e.g., TV sets)<sup>5</sup>, automotive products (car industry)<sup>4</sup>, polymers (polypropylene vs. polyethylene and PVC)<sup>6</sup> and, in very few cases, nanotechnology-based products like carbon nanotubes and nanoparticles (quantum dots or metal oxides)<sup>7-10</sup>. Even though nanotechnology is a recent discipline, a lot of work has already been done worldwide and most of the initial hope and trust into nano-based products have decreased. Nevertheless, the new interdisciplinary matching between nanotechnology and other fields like biology is opening new routes of research and the number and variety of products is increasing within research laboratories. However, this development goes by far too fast with respect to advances in classification and

regulation. Tervonen *et al.*<sup>10</sup> tried to establish several risk categories related to nanotechnology and proposed a methodology to identify and weight some potential risks. The problems of agglomeration, reactivity, functionalization, size, bioaccumulation and toxicity are addressed by a pool of independent experts in the fields of biology, materials science, toxicology and law, in order to establish a profile chart for several types of nanomaterials (MWCNT, CdSe and Ag nanoparticles). A similar study was proposed by Wardak *et al.*<sup>7</sup> who, in addition to risk identification, tried to address the problem of environmental release according to specific uses: e.g., it was estimated that embedding in a dense matrix (nanotubes in a tennis racket) constitutes a minor risk compared to dispersion in a gaseous phase (Ag nanoparticles in aerosol).

The problem of greener synthesis in nanoparticle production and, in particular, the effort for using less toxic and lower amounts of solvent was addressed in a 2007 review paper.<sup>11</sup> The authors were concerned with making a point on recent advances towards a more sustainable and greener synthesis of nanoparticles basing their bibliographic research on the 12 principles of green chemistry introduced by P. Anastas in 1998.<sup>12</sup> In a step forward, the idea of *re-inventing* nanotechnology from a green point of view was recently introduced by P. Anastas *et al.*<sup>8</sup> who provide a conceptual and comparative framework for the most eco-compatible syntheses of some common nanomaterials like ZnO, TiO<sub>2</sub>, Au and Ag nanoparticles and nanotubes. Among several examples, they point out how the synthetic route to Au nanoparticles shifted from an organic solvent-based to a water-based process involving super critical CO<sub>2</sub>. Further efforts in this field allowed the substitution of chemical catalysts by biological ones, like biomolecules (glucose, starch) or whole cells (fungi, bacteria). From a quantitative point of view, they compare the impact of the production of various nanoparticles by using a very simple analytical tool, the E-factor, which is equal to the ratio of the weight of raw material used over the weight of products (Table 1). The authors estimate that the most

eco-disrupting step is the purification of the final product rather than its synthesis: e.g., E-factor related to TiO<sub>2</sub> nanoparticles jumps from 44 to 17.800 when a purification step is introduced. Interestingly, E-factor for biomass-derived gold nanoparticles is very high (29.600) but it is not subjected to modification with purification.

In this context, we questioned ourselves about the relationship between sol-gel and green chemistry. How “green” can sol-gel be? Due to the large number of works using sol-gel as the main technique to synthesize materials (gels, powders, monoliths, thin films), we decided to focus only on the most studied element, silicon, since many aspects that will be covered here can easily be extended to transition metal sol-gel chemistry

Sol-gel has been used as an alternative, wet method to synthesize ceramics and some of the green chemistry principles are intrinsic to the technique itself. In fact, sol-gel synthesis is generally performed at room temperature in a hydro-alcoholic medium in presence of a basic or acidic catalyst. Since 1977, sol-gel is recognized as being a soft chemistry, *chimie douce*,<sup>13</sup> process with respect to classical methods to produce glass at very high temperatures. The idea of the sol-gel process is to use metal alkoxides as molecular precursors and exploit their reactivity in solution towards hydrolysis and condensation in a pH-range between 0 and 10 and at room temperature. The versatility of the technique in terms of processing contributed to its worldwide success.<sup>14</sup> Despite the many positive aspects of sol-gel, several questions concerning its entirely “green” aspect could arise. What is the environmental impact of metal alkoxides and added catalyst? Which is the most energy-saving process? Can sol-gel be performed under solvent-free conditions ?

The twelve principles of green chemistry summarized in Scheme 1 can be gathered into three general categories as shown below.<sup>12,15</sup> The scope of this review is to show which aspects of research in sol-gel over the past 20 years have met the conditions to satisfy these

principles. Provided that a “green thinking” expressed through LCA or ecodesign studies does not exist yet neither in sol-gel-based nor in many areas of laboratory-scale research, we hope that this contribution will introduce a sustainable thinking into the research carried on in this field

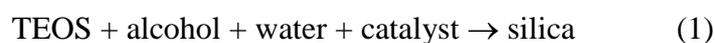
## **2. Silica from TEOS : a case study**

The first silicon alkoxide obtained by the reaction of silicon tetrachloride and alcohol was reported in 1846 by von Ebelman.<sup>16</sup> He observed that the product gelled on prolonged exposure to humid atmosphere. But it is only after 1920 that the sol-gel materials field developed with silica gel dessicants, catalysts and adsorbents.<sup>17</sup> In the late 40's, the monomeric ethyl silicate (former denomination for tetraorthosilicate - TEOS) and its polymers became large-tonnage industrial chemicals manufactured from silicon tetrachloride and ethanol by a continuous process.<sup>18</sup> The hydrolysis of ethyl silicate was used as a convenient process for obtaining an adhesive type of silica. Needs for either acidic or basic catalysts to enhance the rate of hydrolysis and of a mutual solvent to obtain homogeneous reaction were already quoted.<sup>19</sup>

A typical sol-gel reaction to form silica involves hydrolysis of a tetraalkoxysilane  $\text{Si}(\text{OR})_4$ . The most common ones are tetraethoxysilane ( $\text{Si}(\text{OCH}_2\text{CH}_3)_4$ ) and tetramethoxysilane ( $\text{Si}(\text{OCH}_3)_4$ ), which are abbreviated in the literature as TEOS and TMOS respectively. The first one is by far the most used. The keywords "Silica" and "TEOS" lead to more than 2300 citations and only less than 400 when "TEOS" is replaced by "TMOS".<sup>20</sup> This is mainly explained by the cost of each product, TEOS being much less expensive than TMOS, but also by the higher toxicity of TMOS. Silicon tetraalkoxides generally have a low order of toxicity, which may be associated with their alcoholic products of hydrolysis.

Notable exception is tetramethoxysilane, whose vapors may be absorbed directly into the corneal tissue, causing blindness.<sup>21</sup>

Water is not the only reactant that is mixed with TEOS during the sol-gel reaction. Hydrolysis is normally carried out in a mutual solvent since  $\text{Si}(\text{OR})_4$  and  $\text{H}_2\text{O}$  are immiscible. The parent alcohol ROH is usually selected to avoid transesterification reactions, leading to the formation of mixed  $\text{Si}(\text{OR})_{4-x}(\text{OR}')_x$  species. Water is thus no longer a solvent but more a reactant: the  $\text{H}_2\text{O}:\text{Si}$  hydrolysis ratio ( $h$ ) is often less than 10, with a preferred ratio of 4, which corresponds to the stoichiometric amount of water to fully hydrolyze the tetraalkoxysilane molecule. Catalysts are also employed to enhance the rate of reaction that is extremely slow at neutral pH,  $4 \cdot 10^{-6} \text{ l.mole}^{-1} \cdot \text{sec}^{-1}$ , while it increases to  $6 \cdot 10^{-3} \text{ l.mole}^{-1} \cdot \text{sec}^{-1}$  at  $\text{pH} = 1.2$ .<sup>19</sup> Mineral acids or ammonia are most generally used, as well as nucleophiles such as  $\text{F}^-$ . The ingredients of the typical sol-gel reaction that we selected as a case study can thus be summarized as follows:

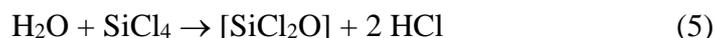


TEOS and its polymeric derivatives account for more than 90 % of the dollar value of nonaaryl- or alkyl-substituted silicon esters.<sup>21</sup> The world production of TEOS can be estimated between 23,000 and 32,000 tons. Pricing ranges from \$2 to \$6 per kg depending on grade and quantity. Some of the major producers are Silbond, Wacker, Evonik and Dow Corning.

TEOS is synthesized in two main ways,<sup>22</sup> either from silicon tetrachloride and ethanol (2) or directly from silicon metal and anhydrous ethanol (3)



*TEOS from SiCl<sub>4</sub>*. As already mentioned, the principal synthetic method from silicon tetrachloride (2) has been described by von Ebelman in 1846.<sup>16</sup> The chemistry of this process is very simple, but this type of reaction has several disadvantages. The co-production of copious amounts of hydrogen chloride necessitates the use of equipment made of expensive alloys and also presents disposal problems. The Si precursor, here silicon tetrachloride, contains a minor proportion of silicon and is rather expensive. Moreover, silicon tetrachloride is readily hydrolysable to produce hydrogen chloride, which makes this reactant difficult to store and handle.<sup>22</sup> Process considerations must also take into account the self-propagating by-product reaction, which results in polymeric species formation.<sup>22</sup>



In the batch production of TEOS, the initial reaction product contains at least 90 wt% of TEOS with 28 wt% SiO<sub>2</sub> content. After distillation, the fraction contains at least 98 wt% of TEOS.<sup>22</sup> Oligomeric versions are also commercially available and referred as ethylsilicate 40 or 50, this last number referring to the SiO<sub>2</sub> wt%.

In the preparation of organosilicon compounds and also in the preparation of highest-grade silicon, silicon tetrachloride is obtained as an unwanted by-product, which can explain why the production of TEOS from silicon tetrachloride is usually part of a larger production process. Productions of SiCl<sub>4</sub> from materials containing SiO<sub>2</sub> (including rice husk) have also been described.<sup>23,24</sup>

*TEOS from Si*. The catalyzed direct reaction of ethanol with silicon metal in the presence of high-percentage alkali ethylate solutions (eq. 3) is known since the late 40's.<sup>25,26</sup> Improvements of reaction rates and yields have been investigated, leading to the development

of more efficient catalysts.<sup>27</sup> This process becomes an important commercial technology in the 1990s for production of lower esters. Here the selected silicon precursor is certainly the most suited one to fulfil one of the 12 principles of Green Chemistry that is atom economy. But the technology used to produce silicon does not necessarily fulfil all the principles, especially in terms of energy efficiency. Silicon is commercially produced by carbothermal reduction of silica in a high temperature, capital equipment and energy intensive process. High-purity silica reacts with a carbon source (wood, charcoal, coal..) in an electric arc furnace using carbon electrodes at  $T \geq 1700^\circ\text{C}$  according to the following reactions:



The silicon produced via this process is called *metallurgical grade silicon (MG-Si)* and is at least 98 % pure. No one really knows how much of MG-Si is being produced worldwide. Volumes from 1.7 to 1.9 millions tons are estimated.<sup>28</sup> Around 50 % is used in the aluminium industry, 40 % as raw materials to produce silicone, and the remaining 10 % for the photovoltaic and semiconductor industries that require high-purity silicon. For many years, there was an abundance of MG-Si, but in recent years, demand has drawn closer to supply. Prices have almost doubled in recent years, and in September 2008, metallurgical grade silicon cost about \$3.2/kg. More recently, new electrochemical processes which can provide cheaper and easier production of Si metal directly from silica, without any CO<sub>2</sub> emission and at much lower energy have been described.<sup>29</sup>

*EtOH in TEOS production.* Ethanol is derived from two main processes, hydration of ethylene or fermentation of sugars, which are the respective primary methods for production of industrial ethanol and beverage alcohol. Current technology for industrial ethanol involves the utilization of a porous support impregnated with phosphoric or tungstic acid that act as

catalysts. Ethanol for use in alcoholic beverages, and the vast majority of ethanol for use as fuel, is formed through fermentation of a variety of starch or sugar-based feedstocks, such as corn and grain sorghum.<sup>30</sup> Sugars can also be obtained from cellulose, even if it is more difficult to break down cellulose to convert it into usable sugars for ethanol production.<sup>31</sup> Yet, making ethanol from cellulose dramatically expands the types and amount of available material for ethanol production. This includes many materials now regarded as wastes requiring disposal, as well as corn stover, wheat and rice straw, wood chips or energy crops of fast-growing trees and grasses.

Which of the two processes is more economical depends upon the prevailing prices of oil and of grain feed stocks. World production of fuel ethanol in 2006 was 51 ggalitres with 69 % of the world supply coming from Brazil and the U.S.A. The U.S. federal government gives ethanol producers a tax credit and mandates their fuel to be blended into the nation's gasoline supplies. The Renewable Fuel Standard program will increase the volume of renewable fuel required to be blended into gasoline from 9 billion gallons in 2008 to 36 billion gallons by 2022.<sup>32</sup> Interestingly, this tax credit has also been extended to TEOS production through various amendments to the Internal Revenue Code.<sup>33</sup>

### **3. Alternative precursors**

#### **3.1 Aqueous precursors**

Silicates, mainly in the form of aqueous alkaline sodium silicate solutions (« waterglass ») were used for the synthesis of silica prior to silicon alkoxides.<sup>34</sup> Sodium silicates are prepared by the fusion of silica sand with soda ash (sodium carbonate) or sodium hydroxide at 1,100-1,200°C, the resulting molten salt being then dissolved into water.<sup>35</sup> During this process, it is

possible to vary the Na:Si ratio that will determine the nature of silicate species in the solution. Silicates are widely used as such in the soap and detergent industries. They constitute a starting product for the synthesis of colloidal silica by acidification, either via sulfuric acid addition or via an ion exchange resin. Silicates are also used in the formulation of adhesives, paints and cements.

As previously mentioned, the development of sol-gel technology has been mostly related to alkoxide-based chemistry. Only recently silicate-based processes were re-investigated in the context of green sol-gel chemistry,<sup>36</sup> because they are non-toxic aqueous precursors with low environmental impact that can be used under solvent-free conditions.<sup>37</sup> In some cases, silicates and alkoxides can be used almost indistinctively as illustrated by the preparation of organized mesoporous materials.<sup>38</sup> Interestingly, it is possible to use mixtures of sodium silicate and organosilanes to obtain organically-modified materials in a single step.<sup>38b,c</sup> Silicate-based hybrid nanoparticles incorporating synthetic or natural polymers have also been recently described,<sup>39,40</sup> sometimes with targeted applications in the field of drug delivery.<sup>41</sup> When the use of alcohol as a co-solvent or its generation by hydrolysis reaction is a problem, silicates may even be superior to alkoxides, as demonstrated in the field of the sol-gel encapsulation of living cells.<sup>42</sup>

However, when compared to silicon alkoxides, silicates exhibit a number of limitations. Indeed, silicate solutions contain a high number of poly-silicic acids (or silica oligomers) whose structure has been extensively studied by <sup>29</sup>Si NMR.<sup>43</sup> Such a diversity of oligomers, that in fact represent the molecular precursors involved in the silica polymerization reaction, constitutes one of the major differences between silicates and alkoxides. Indeed, a key feature of the sol-gel process is that it can be controlled through the hydrolysis of a well-defined alkoxide precursor. Such a control, in principle, is no longer possible with silicates that do not possess labile Si-OR groups. However, upon dilution, oligomers tend to de-

condense through a hydrolytic cleavage of a Si-O-Si bond.<sup>34,44</sup> This means that it is possible to exert some control over the nature of silicate precursors, although, to our knowledge, this approach has not been really investigated. In parallel, it is worth noting that the impact of the diversity of oligomers on the chemical reactivity of aqueous silicate solutions has been poorly explored. In this context, recent studies revealed that the degree of condensation of poly-silicic acids directly influence their ability to interact with biopolymers.<sup>45</sup> This influence is partly due to the fact that poly-silicic acids exhibiting various structures (linear, cyclic) and oligomerization degrees will bear a different negative charge at  $\text{pH} > 3$  and are therefore expected to show variable ability towards hydrogen bond formation and electrostatic interactions. Noticeably, silica oligomers are also formed during the sol-gel reaction of silicon alkoxides but they are much less reactive towards hydroxylated or positively charged biopolymers, probably because hydrolysis is not complete and some of the silanol groups are still in the Si-OR form.

The charge of the oligomers, together with the presence of the sodium ions, also has a strong impact on the possibility to form silica gels. A typical procedure involves the addition of a mineral acid to the alkaline silicate solution. First, because the addition of salts not only speeds up the gel formation kinetics but also shifts the pH of minimum gelation time to higher values,<sup>34</sup> it is not possible to prepare gels at neutral pH with concentration above *ca.* 0.8 M. Moreover, these gels contain a high amount of sodium salts. The problem can be partially overcome by passing the sodium silicate solution over an acidic ion exchange resin, resulting in a sodium-free solution. However, direct gelation of the solution during the exchange process often occurs for silica concentration over *ca.* 1.2 M. As a comparison, TEOS-based gels prepared in the absence of ethanol as a co-solvent can be obtained at concentrations up to 2M. Finally, the condensation degree of the silica gel obtained from sodium silicate is lower

than for silicon alkoxides and decreases with increasing amount of sodium, which is expected to result in a lower mechanical and chemical stability.<sup>46</sup>

Thus, a critical assessment of the possible use of aqueous silicates as alternative precursors to TEOS or TMOS suggests that not only the former are more advantageous from an environmental point of view but also that their reactivity is close enough to the latter to be used in many applications. In fact, the main limitation of these aqueous sources, besides the poorer mechanical and chemical stability, is probably that they are only compatible with water-miscible solvents and molecules. Overall, it appears that the supremacy of silicon alkoxide-based processes has long been detrimental to the development of an aqueous silicate-based chemistry applied to advanced materials design. The recent renewed interest for these precursors, mainly triggered by environmental/economical concerns, is, to our point of view, full of promises for the future of the silica-based sol-gel technology.

To close this section, it is worth mentioning that silica sols may also be used as aqueous precursors for the synthesis of silica.<sup>34</sup> However, because they are prepared from sodium silicate or silicon alkoxides, colloidal silica can be considered as a secondary source of precursor and will not be discussed in more details here.

### **3.2 Alternative precursors from SiO<sub>2</sub>**

As mentioned above, the alternative route to the use of alkoxides considers direct dissolution of silica into silicates. Strong bases, like NaOH, or highly nucleophilic catalysts, like F<sup>-</sup>, easily dissolve silica, constituting the easiest way to achieve such a goal. Despite their efficiency, alternative conditions have been developed to avoid the synthesis of highly reactive silicates under strong pH conditions or the use of dangerous fluorine-based chemicals, like HF. The group of Laine was very active in the synthesis of silicon compounds

using ethylene glycol (EG) and alkylamino compounds directly starting from different forms of SiO<sub>2</sub> (sand, fumed silica or silica gel). Addition of EG to silica in presence of a strong base allowed the formation of penta-coordinated compounds<sup>47</sup> which have the advantage, with respect to hexacoordinated catechol-based ones, of being a better intermediate to silicon precursors due to its reactivity: e.g., treatment with HCl gas provides a mixture of water-soluble tetra-coordinated silicon isomers which can be used as substitutes to TEOS (Scheme 2).

Improvement of this reaction scheme was proposed few years later, following an early work of Frye on silatranes,<sup>48</sup> in which silica was reacted with triethanolamine to produce the corresponding amine-stabilized silicate oligomers. When ethylene glycol is added to the system, reaction seems to be under a stricter control to form a pentacoordinate silatrane glycol,<sup>49</sup> as shown in Fig. 2, where the Si atom is coordinated by the bulky triethanolamine group. The compound is resistant to hydrolysis over a week period and the synthesis is easily up-scalable. The low toxicity of triethanolamine makes it a much suitable reagent than strong bases, whose stoichiometric amount with respect to silica constituted the main problem of the previous approach. Finally, reactivity of silatranes can be modified if EG is exchanged with similar compounds like diethylene glycol or allyl alcohol.<sup>49c</sup>

A new step in the synthesis of water-soluble neutral precursors from silica was introduced by Cheng *et al.*,<sup>50</sup> who demonstrated that stoichiometric amount of the amines is actually not needed when an excess of EG is used. In fact, catalytic quantities ( $\sim \mu\text{M}$ ) of either triethanolamine, triethylenetetraamine or alkali base are largely sufficient to promote silica dissolution. In addition, the efficiency of the experiment could be tested in presence of both pure and processed (common antifreeze is used) EG on large quantities of SiO<sub>2</sub> at temperatures above 200°C to distillate off the un-reacted EG. Overnight experiments indicate that dissolution kinetics and yields were better with metal hydroxides than with amines, due

to their stronger basicity. However, although the pKa of evaluated amines differs by three orders of magnitude, the dissolution kinetics and yields were comparable.

Synthesis of saccharide-silicate complexes was reported by Lambert *et al.*,<sup>51</sup> inspired by Kinrade *et al.*<sup>52</sup> who used polyols to form five and six-coordinated aqueous silicates. In particular, *D*-fructose coordinates to silicic acid by the formation of a *cis*-HO-C-C-OH stabilized pentacoordinated planar complex. The *cis* position of the two OH groups in fructose is necessary to achieve this configuration. An extension to this work showed that when *D*-fructose is used in presence of a weak amine, triethylenetetramine, and EDTA (to complex metal cations), sand can be partially dissolved at ambient pressure in a 1 to 4 h time period and at temperature below 100°C to give silica particles.<sup>53</sup> Even if no precursor is actually achieved in this case, the strategy seems to open a new way to achieve a complete silica dissolution.

### **3.3. Alternative precursors from TEOS**

We have previously discussed alternative ways of producing silicate monomers from silica under mild conditions. Since alkoxysilanes are obtained from silica *via* a number of reaction steps, the question is: why transforming alkoxysilanes further ? Two main drawbacks are associated to these compounds: water immiscibility and release of alcohols. In the first case, an organic co-solvent, like ethanol, is generally added, limiting the possibility to establish a solvent-free synthetic procedure. Secondly, considering the large number of bio-related (protein, enzyme, bacteria encapsulation) applications of sol-gel derived silica materials, ethanol is not fully suitable due to its toxicity and protein denaturation effect. In addition, mechanical properties are generally affected by alcohol evaporation. Corresponding gel

shrinkage is also an issue. To overcome these problems, some groups proposed chemical modifications of common alkoxides.

An early work of Mehrotra demonstrated the exchange of alkoxides groups with four equivalents of ethylene glycol.<sup>54</sup> However, the poor stability towards hydrolysis of these compounds prevented their use for many years until recently. In fact, their strong reactivity in water turned out to be a positive point because catalysis was not necessary anymore. In addition, hydrolysis releases EG, which is a biocompatible compound though not devoid of toxicity,<sup>†</sup> and which can act as a structural stabilizer in the synthesis of silica gels.<sup>55</sup> The group of Hüsing reported a large number of works showing the synthesis of crack-free silica gels with multi-scale porosity when a porogen is used.<sup>56</sup> In parallel, Shchipunov *et al.* demonstrated the compatibility of this precursor with a large number of polysaccharides to form hybrid organic/inorganic silica gel in the absence of a catalyst, because some polysaccharides were found to accelerate the sol-gel reaction kinetics.<sup>57</sup>

Additionally to EG, other polyols, including saccharides, have been evaluated to synthesize monomeric silicon-based compounds, as shown in Scheme 3. Gill and Ballesteros used glycerol-modified TMOS to obtain a poly(glyceryl silicate) “SiO<sub>1.2</sub>Glc<sub>0.8</sub>” precursor which was used to make gels for biomolecule and cell encapsulation.<sup>58</sup> Besides the final material application, glycerol is an interesting by-product obtained from biodiesel production and its use in the synthesis of sol-gel material could be a cheap and interesting way to recycle it.

Brook *et al.* also used polyols and, in particular, sugars (sorbitol, maltose and dextran) to modify TEOS and TMOS into precursors like maltosylsilane and dextrysilane or gluconamidyltriethoxysilanes (GLS) and maltonamidyltriethoxysilanes (MLS).<sup>59</sup> In the first case, modification takes place directly over the alkoxy silane, while in the second case,

reaction actually occurs between tripropylamino-modified ethoxysilane and glucose to form a stable non-hydrolysable imine bond between the aldehyde and the amine groups.

### **3.4. Alternative silica sources**

The previous sections have shown how to derive silicate precursors directly from SiO<sub>2</sub> or from alkoxysilanes. In all cases, SiO<sub>2</sub> originates directly from sand. Alternatively, silica can be extracted from higher plants and, in particular, from *Gramineae* that transform silicic acid into SiO<sub>2</sub>, which is accumulated up to 20 wt%.<sup>60</sup> Rice (*Oryza sativa*) belongs to the *Gramineae* family and its silicic acid uptake is one of the most efficient in nature. In particular, rice husk has always been regarded as a potential unlimited silica source. Interestingly, rice husk is a by-product of the rice industry and it is commonly considered to constitute an environmental issue to deal with rather than a primary source of matter. Many scientists have processed rice husk, which is generally calcined into ash to eliminate the organic part and keep the amorphous silica residue instead. Nevertheless, most of the studies have tried to use rice husk ash (RHA) as a material itself rather than a potential source of silica. The number of works in which rice husk ash is used “as such”, mainly as filler in cements or as adsorbent, is very high and the topic is out of the goals of this article. Instead, we show few examples in which rice husk and rice husk ash have been used as primary silica sources. Of course, no changes occur from the chemistry point of view, but the approach is interesting because of the full recyclability of the source.

A patent deposited in 2002 describes a way of extracting silica using a classical treatment in basic medium (generally a 10 wt% NaOH solution) at temperature between 100 and 200°C.<sup>61</sup> In order to recover silica directly from the solution by precipitation, sulfuric acid is added drop wise to the hot basic solution. A similar method is used by Kalapathy *et al.*, who treated rice husk ash with 1N solution of NaOH for one hour.<sup>62</sup> The extracted sodium

silicate was then employed in the synthesis of silicate films, whose strength and flexibility varies with respect to the amount of NaOH content. Films were used as barriers to separate polar from non-polar organic solvents in the vapour phase.

Sanchez-Flores *et al.* used glycerol to depolymerise RHA and form glycerol-containing silica gels having pores in the mesoscopic range.<sup>63</sup> The same depolymerisation technique is used in the synthesis of zeolite ZSM-5, where RHA and glycerol are reacted with a natural zeolite, clinoptilolite, as a source for tetrahedral aluminium.<sup>64</sup> Finally, mesoporous MCM-41 was synthesized using the classical recipe where a surfactant is used as a porogen while SiO<sub>2</sub> is extracted from RHA.<sup>65</sup>

Another original procedure, not only more energy-saving than previous ones but also leading to a less usual form of silica precursors, was recently reported.<sup>66</sup> In this case, a methanolic solution of choline hydroxide or tetramethylammonium hydroxide was used in presence of rice husk ash at room temperature to obtain silsesquioxanes, that is molecular cages of siloxanes, over one month time period. Temperature and base concentration increased the efficiency of the dissolution process. The obtained molecular cages can further react to produce novel hybrid organic-inorganic building blocks.<sup>67</sup>

## **4. Alternative solvents**

### **4.1 Water**

There is, in principle, no limitation in the use of water as the only solvent for the sol-gel reaction of TEOS or TMOS. The fact that these alkoxides are not miscible with water indeed require an activation of the hydrolysis step that release parent alcohol molecules that allow the formation of a homogeneous mixture (« hydrosol »). This can be easily achieved by

the addition of an acid catalyst and a suitable stirring/activation source such as ultrasound (see also section 5).<sup>68,69</sup> However, it was already mentioned that one of the main advantages of using silicon alkoxide rather than aqueous silicates is that the sol-gel reaction, and therefore the final structure of the silica gel, can be controlled through the hydrolysis ratio  $h$ . An excess of water limits this possibility so that the kinetics of gel formation become independent of  $h$ .<sup>68</sup> This might explain why these conditions were not studied in details.<sup>14,70</sup> It is nevertheless worth mentioning that silica hydrogels formed with high  $h$  ratio (up to 50) were recently described for the purpose of cell immobilization.<sup>71</sup> As expected, it was found that the density of the xerogels (after supercritical drying) decreases with increasing  $h$ . However, intermediate  $h$  values were found more suitable to form homogeneous and mechanically stable materials in the presence of poly-ethylene glycol, suggesting some critical  $h$  value related to phase separation phenomena.

As mentioned for silica aqueous precursors, it is very likely that water-based sol-gel reactions will attract more interest in the years to come in the context of Green Chemistry. One particular field where the poorly-controlled hydrolysis of silicon alkoxides in water may become crucial is the chemical modification of nanoparticle surface. This is usually performed in organic solvents (such as toluene) to avoid pre-polymerization of the grafting moieties and favor their hydrolysis/condensation on the hydrated layer of silanols present on the particle surface.<sup>72,73</sup> First studies of organoalkoxysilane grafting on colloidal silica in ethanol/water mixture suggest that the presence of an excess of water does not prevent covalent bonding between surface silanols and mono- or di-functional ethoxysilane.<sup>73b</sup>

Another situation where water is the only solvent for the sol-gel reaction can be found when alkoxide precursors are used in the vapor phase.<sup>74</sup> This technique was particularly applied for silicification of biopolymer-based hydrogels.<sup>75</sup> Such an approach is very useful when the mixture of the polymer solution with the alkoxide in solution is not possible under

stirring because it is too viscous or should not be disturbed, as demonstrated for collagen/silica composites.<sup>76</sup>

## 4.2. Ionic liquids

Ionic liquids (IL) are considered as promising solvents for Green Chemistry mainly due to their very low vapor pressure that limits the release of volatile organic compounds (VOCs) in the atmosphere.<sup>77</sup> Moreover, they have been used as versatile and efficient solvents for many organic and inorganic reactions.<sup>78</sup>

In the field of silica sol-gel chemistry, ILs have first been used by Dai *et al.* as a solvent and a drying control chemical additive (DCCA) to obtain porous materials.<sup>79</sup> In this case, the starting mixture is free of water (non-hydrolytic sol-gel: NHSG) and contains TMOS, IL and formic acid as an acid catalyst. This approach was further applied to hybrid materials,<sup>80</sup> and applied to molecularly imprinted monoliths.<sup>81</sup> Hydrolytic reactions have also been developed incorporating IL, often involving additional alcohol.<sup>82,83</sup> The effects of IL on silica porosity and morphology were reported.<sup>84,85</sup> Interestingly, the authors recently suggested that ILs may act as catalysts for the sol-gel reaction due to the Bronsted acid and Lewis base character of the cationic and anionic components of the IL, respectively. Because IL can exhibit self-assembly properties,<sup>86</sup> they have been used for the synthesis of periodic mesoporous silica.<sup>87-90</sup>

Indeed, when porous materials are targeted, it is necessary to withdraw the IL template to get access to the porosity. This is usually performed by solvent extraction but supercritical drying procedure in CO<sub>2</sub> (see below) was recently proposed as a convenient alternative.<sup>85</sup> However, it may also be interesting to preserve the IL component inside the silica matrix. These materials, described as « ionogels » combine the advantages of the silica network (mechanical stability, transparency) while maintaining key properties of the IL (thermal

stability, ionic conductivity) (Fig. 3).<sup>91</sup> Another fascinating feature of ILs is their good compatibility towards enzymes. Thus, significant improvements in the catalytic activity of several enzymes in IL/silica materials were reported.<sup>92-94</sup>

To our knowledge, no attempts to associate IL with aqueous silicates have been reported so far. In contrast, mixtures of colloidal silica with IL were shown to form gels even at low silica loading (2-3 wt%).<sup>95</sup> As an alternative, it is possible to synthesize organically-modified precursors where the cationic (imidazolium) component of the IL is covalently linked to a silicon atom, and use them to graft silica nanoparticle surface.<sup>96</sup> Such precursors can also be used for the deposition of IL/silica films via a NHSG process, that were evaluated for the accumulation of electroactive anions on ITO electrodes.<sup>97</sup> Very recently, it was possible to prepare alkoxysilanes that bear the anionic component of the IL (sulfonimide). Addition of a traditional templating surfactant, such as CTAB or P123, to a mixture of TEOS and both cationic/anionic IL precursors leads to periodic mesoporous materials whose self-organization is driven by specific IL precursor/surfactant interactions and that contain ion pairs on their pore surface.<sup>98</sup>

This rapid overview indicates that the association of silica sol-gel with ionic liquids has already been fruitful for the elaboration of novel materials. ILs can be used as alternative solvents, especially using NHSG reactions, and may act as catalysts for the sol-gel reaction. They also contribute to improve silica material properties such as ionic conductivity or biological compatibility. However, although they appear as useful and versatile porogens, their environmental benefit when compared to other traditional templates is not clear, especially considering the conditions of extraction. In addition, the toxicity and detrimental environmental impact of the reagents involved in their synthesis and, more importantly, of the common ILs themselves are now well-identified,<sup>99</sup> so that the future contribution of ionic

liquids to green chemistry in general, and sol-gel chemistry in particular, may need to be reconsidered.

### 4.3 Supercritical fluids

The history of the association of supercritical fluids (scF) with sol-gel chemistry is more than 70 years old,<sup>100</sup> and has been regularly reviewed over the past ten years.<sup>101-104</sup> The interest in scF was initially triggered by the need for a suitable method to dry gels while avoiding loss of the porous structure due to capillary stress occurring during solvent evaporation. This problem can be overcome using scF for which no liquid-vapour interface, and therefore no capillary pressure, exists. Resulting materials, called « aerogels », can show surface area larger than  $1000 \text{ cm}^2 \cdot \text{g}^{-1}$  and pore volumes greater than 95 %. They can be made transparent and have found many applications in physics, space and life sciences.

First aerogels were prepared from hydrogels based on sodium silicate solutions in which water was exchanged for alcohol that was used as the source of scF.<sup>100</sup> Similarly, when the technique was applied to alkoxy silane-based sol-gel technology, the supercritical fluid was the ethanol (or methanol) solvent added to TEOS (or TMOS) in the presence of water, containing acid or base catalysts.<sup>105</sup> The gel can be first formed and then dried in corresponding sc conditions, or the mixture in the sol state can be directly introduced in the autoclave. However, both alcohols show high critical temperatures ( $> 200 \text{ }^\circ\text{C}$ ) and may react with silica during the drying process.<sup>104</sup> This problem can be overcome by using acetone as the reaction solvent,<sup>106</sup> or by exchanging alcohol by another solvent such as acetonitrile in a two-step process.<sup>107</sup> In parallel, an alternative approach using  $\text{scCO}_2$  whose critical point is close to room temperature ( $T_c = 31.1 \text{ }^\circ\text{C}$ ) and at moderate pressure ( $P_c = 73.9 \text{ bar}$ ) was developed.<sup>108</sup> In this case, the gel is first saturated with the organic solvent that should be

exchanged for liquid or sc carbon dioxide before extraction. Noticeably, a catalytic effect of scCO<sub>2</sub> on the silica gel formation was reported.<sup>107</sup>

More recently, scFs have been recognized as alternative solvents for the synthesis of organic and inorganic materials.<sup>109</sup> In this context, the use of scCO<sub>2</sub> as the only solvent of the sol-gel reaction (*i.e.* without alcohol addition) was described (Fig. 3).<sup>110</sup> Because water is not miscible with scCO<sub>2</sub>, a NHSG process starting from an alkoxysilane/formic acid mixture was developed and applied to both pure silica and hybrid materials. Other acid catalysts were further evaluated but sometimes required acetone addition for solubility purpose.<sup>111</sup> This approach was also useful to prepare nanocomposites either by scCO<sub>2</sub>-mediated gelation of silica in the presence of preformed polymers or by the direct co-polymerization of an organic and an inorganic network.<sup>112-114</sup>

Similar to ionic liquids, scCO<sub>2</sub> appears as a green alternative to alcohol solvents because it is not inflammable (less chemical hazards) and it does not release VOCs (limited environmental impact). Indeed, carbon dioxide emission in large amounts is to be avoided but systems allowing the recovery and recycling of CO<sub>2</sub> have been suggested.<sup>104</sup> Noticeably, another powerful method to synthesize aerogel-like materials has been described. It takes place at room temperature and ambient pressure without requiring scF, but usually involves chemical modification of the silica gel.<sup>115</sup> Comparing both approaches, the scF route is clearly more environment-friendly, whereas the ambient condition route appears more economically sound. Thus, as a common trend in the field of eco-conception, the future of silica based-aerogels will result from a balance between these two factors.

## **5. Catalysis and activation**

### **5.1. Biocatalysis**

Biocatalysis, *i.e.* the use of a biochemical reaction, either enzymatic or cellular, to enhance the efficiency (rate, specificity) of a chemical reaction has been long used in organic chemistry and biotechnological devices. In the field of materials science, its development is very recent and was triggered by the sudden interest of inorganic chemists for biomineralization processes.<sup>116</sup> Focusing on silica, the shells of diatom algae and the spicules of sponges are now considered as paradigms of hierarchically-organized nanostructured materials.<sup>117,118</sup> Therefore, many studies have been dedicated to the understanding of the biological synthesis of silica.<sup>119,120</sup> It was soon realized that diatoms and sponges are using an aqueous sol-gel route, starting from silicic acid  $\text{Si}(\text{OH})_4$  uptaken from the surrounding water to elaborate a hydrated silica network whose composition is very similar to the typical silica gel obtained from *in vitro* sol-gel synthesis.<sup>121,122</sup>

Interestingly, these two organisms have selected different principles to activate silica formation. In the case of sponges, a protein called silicatein  $\alpha$  was extracted from the siliceous spicule, that bears strong sequence similarity with a hydrolytic enzyme cathepsin L.<sup>123</sup> The main difference between the two proteins is found in the active site where an initial cysteine-histidine pair is changed for a serine-histidine. The presence of hydroxylated serine allows the immobilization and activation of a silicon alkoxide molecule whereas the free electron pair of the histidine imidazole ring favors its hydrolysis, following a nucleophilic activation (Fig. 4a). Further investigations revealed that silicatein  $\alpha$  could be considered as an enzyme towards the hydrolysis of Si-OR bonds.<sup>124</sup> In contrast, silica formation by diatoms is not an enzymatic process but involves polycationic molecules, either proteins (silaffins) or linear polyamines.<sup>125</sup> In this case, the activation process involves both an acid/base reaction between ammonium groups and silanols as well as an enhancement of condensation rate due to the local concentration of silicates via electrostatic interactions (Fig. 4b).<sup>126,127</sup>

Silicatein  $\alpha$  is therefore a very good candidate for biocatalytic formation of silica and was used to form gels or films.<sup>128</sup> It could be expressed in *Escherichia coli* bacteria and applied for cell encapsulation.<sup>129</sup> In parallel, small amino-alcohol or amino-thiol molecules mimicking silicatein  $\alpha$  active site were found to efficiently activate silica formation.<sup>130</sup> While silaffins as such were not further studied for material synthesis, small peptide sequence derived from the proteins, and in particular the R5 molecule (H<sub>2</sub>N-SSKKSGSYSGSKGSKRRIL-COOH) were used to activate silica formation, finding applications in holographic devices and enzyme encapsulation.<sup>131</sup> Polyamines, either natural or synthetic equivalents such as poly-lysine, poly-ethyleneimine, poly-allylamine or amine-terminated dendrimers, also efficiently induce silica precipitation, as nanospheres, fibers or platelets.<sup>132</sup> This ability of polyamines was used to grow silica layers on surface-modified glass substrates,<sup>133</sup> and even to coat polymer microbeads.<sup>134</sup>

In parallel, efforts have been made to find other enzymes that are not found in silicifying organisms but that may have some chemical activity towards silica precursors. First report in this area was dedicated to a lipase enzyme that catalyses the hydrolysis of triglycerides into fatty acids and glycerol. Lipases can also hydrolyze phospholipids and synthetic esters. Thus, it was proposed that such enzymes could also contribute to the hydrolysis of silicon alkoxides (TMOS).<sup>135</sup> More recently, a number of other enzymes, and in particular proteolytic enzymes  $\alpha$ -chymotrypsin and trypsin were shown to favor silica gel formation from TEOS.<sup>136</sup> Interestingly, these two enzymes are serine proteases whose active site includes a serine-histidine pair, similarly to silicatein  $\alpha$ .

Among available bio-related catalysts, the latter enzymes are probably the most interesting in the field of green sol-gel chemistry as they are natural molecules available in large quantities that are active in aqueous solutions at room temperature. One limitation of this approach is the limited pH range where these specific enzymes are active although it

might be possible to find suitable enzymes adapted to different acidity/alkalinity conditions. Another aspect to be mentioned is that proteolytic enzymes are effective for silicon alkoxide hydrolysis but they probably do not favor aqueous silicate condensation, as already shown for silicatein  $\alpha$ .<sup>123</sup> But the key concern when using these molecules, and all other candidates presented above, is that they remain trapped in the silica gel they have contributed to form, meaning that they cannot be recovered. This is indeed a major drawback from an economic point of view and may also have impact on the possibility to simultaneously dope the silica gel with other species since biocatalyst-dopant unfavorable interactions may arise. Nevertheless, the field of biocatalysis applied to inorganic material synthesis is still in its infancy so that there is hope for further improvements in a next future.

## **5.2 Ultrasound and microwave techniques**

As an alternative to bio/chemical catalysis, physical activation of the hydrolysis/condensation reactions of silica precursors via external power sources has been explored. In particular, the application of sonochemistry to sol-gel chemistry has been extensively studied, based on the pioneer works by Zarzycki and Esquivias.<sup>137</sup> When a liquid is submitted to ultrasound radiation, acoustic cavitation arises, resulting in the growth and collapse of bubbles. This collapse leads to a local intense heating and pressure (hot spot) that can activate a chemical reaction, including organic polymerization and organometallic conversion to metal colloids, and also create shockwaves that enhance the velocity of soluble or suspended species.<sup>138</sup>

As mentioned above, one of the main reasons for adding alcohol in the conventional sol-gel process (eq. 1) is that traditional silicon alkoxides are not miscible with water whereas the alcohol is a common solvent for both the chemicals. Thus, mixture of TEOS or TMOS with water consists of a two-phase liquid until ethanol or methanol release during hydrolysis

leads to a homogeneous solution. To enhance this reaction, rapid mechanical stirring can be used to obtain a water-in-oil emulsion with the minimum droplet size (*i.e.* maximum surface contact). It was found that sonication was a very efficient alternative to increase the homogenization rate, both because it favors water droplet dispersion and locally activates the hydrolysis reaction, via a radical mechanism.<sup>139</sup> Overall, a drastic decrease in gelation time is observed when compared to traditional routes. In terms of structure, these materials, termed sonogels, are denser than gels obtained in alcoholic solutions, as they exhibit smaller primary nanoparticles with a more limited dispersity in size. This higher level of cross-linking may also be related to the fact that the evaporation of alcohol released during hydrolysis is favored in these conditions. This approach could be applied to pure silica, organic- and inorganic-doped gels as well as to hybrid (sono-ormosils) materials.<sup>137</sup> It can be used to decrease the size dispersity of silica nanoparticles formed using the Stöber reaction, thus constituting an interesting alternative to surfactant-based process, although larger particles are obtained due to colloidal agglomeration.<sup>140</sup>

Noticeably, all previous examples used additional catalysts, *i.e.* the hydrolysis water contained HCl or weaker acids such as oxalic acid (which is toxic by ingestion). Very recently, a catalyst-free method for silica gel formation from TEOS was reported and extended to the synthesis of various hybrid materials (Fig. 3).<sup>141</sup> Indeed, the process has a strong impact on the sol-gel reaction. In particular, it was observed that only hydrolysis and not condensation occurs under sonication. However, the current process presents a major drawback as some unreacted TEOS remains in the solution and must be withdrawn before gel formation.

Microwave irradiation is also a possible method to enhance the kinetics of silicon alkoxide hydrolysis in the absence of added alcohol. In this method, a fast and homogeneous heating is obtained due to the thermal conversion of the oscillations of polar species under

electromagnetic waves.<sup>142</sup> Water is the preferred media for microwave synthesis because of its suitable dielectric properties. Since the hydrolysis reaction involves water both at the molecular (conversion of Si-OR to Si-OH) and macroscopic levels (w/o emulsion), it is not surprising that the sol-gel reaction is very sensitive to microwave irradiation.<sup>143</sup>

A first study conducted by Komarneni *et al.* demonstrated that TEOS-water mixtures without catalyst formed gels within 2 h at 140°C in hydrothermal-microwave conditions, whereas traditional heating conditions (water bath, oven) at 60°C required 2 days or more.<sup>144</sup> The same authors also pioneered the microwave-assisted synthesis of zeolites and mesoporous materials.<sup>145</sup> The technique was also applied for hybrid membrane preparation.<sup>146</sup>

The microwave irradiation can be performed at different steps of the reaction: (a) sol preparation, (b) gelation/ageing and (c) drying/curing, resulting in a significant shortening of the whole synthetic procedure from days to hours.<sup>147-149</sup> The process is not detrimental to the structure of the material and may even enhance its thermal stability,<sup>147</sup> or lead to novel organizations.<sup>150</sup>

Thus, both ultrasound and microwave irradiation allow to perform the silica sol-gel reaction without added alcohol and with a significant reduction of reaction time. They can be applied to both silicon alkoxides and aqueous silicates.<sup>151,152</sup> Considering possible scaling-up, large ultrasonic devices (> 1 m<sup>3</sup>) with high power output (1000 W) are commercially available (Hielscher Ultrasonics). Smaller oven volumes are reached for microwave devices (Anton Paar GmbH). Continuous flow systems have been designed to overcome this limitation (MLS GmbH) but they are clearly not adapted to bulk gel materials. Finally, even if it is now well-accepted that ultrasound is not harmful for human health as long as there is no direct contact between the human body and the irradiated media,<sup>153</sup> the possible detrimental effects of microwave radiation are still a matter of debate.<sup>154</sup>

To end this section, it is worth mentioning that, over the last decade, many efforts have been devoted to the use of electrochemistry for the formation of sol-gel silica.<sup>155</sup> This approach, that relies on a modification of pH at the vicinity of an electrode,<sup>156</sup> has mainly been applied to thin films so that it will not be further discussed here.

## **6. Silica templating : the example of mesostructured materials**

### **6.1. Mesostructured materials synthesis**

Since 1992,<sup>157</sup> a huge number of works has been devoted to the synthesis of organized mesoporous materials (OMM).<sup>158-161</sup> The relevance of such materials in the field of green chemistry has been mainly related to their use in heterogeneous catalysis. However, another aspect of the relationship between OMMs and environmental issue is related to their environmental impact. So the question we wish to address here is: is the conception of these materials *green*?

The answer is definitely negative. In fact, almost all studies published so far focused their attention on the *structure vs. properties* dualism where ecoconception concerns are limited or non-existing. Synthesis of silica-based mesostructured materials generally starts from alkoxysilanes (usually TEOS) or, in some cases, from sodium silicates or silica as inorganic sources. Synthesis of powders generally takes place in aqueous solution while in the synthesis of thin films and spray-dried spheres organic solvents, like ethanol, may actually be added to the initial sol. For a review on aqueous and organic-based synthesis, one can refer to Ref. 161. Solution pH is a very important factor in the synthesis of mesostructured materials. Synthesis under basic pH conditions provides the well-known MCM-41 material<sup>157</sup> while acidic pH conditions were used in the synthesis of the SBA family materials.<sup>162,163</sup> Finally, molecules with surface-active properties, i.e. surfactants, are by far the most exploited templates.<sup>161</sup> The criteria of ultimate choice was purely physico-chemical (critical micelle

concentration and cloud point values, hydrophilic/hydrophobic balance, packing parameter or simply commercial availability) and the main strategies to remove them from within the oxide are relatively limited: calcination or reflux washing in ethanol or ethanol/HCl mixtures are usually performed, although other methods such as ozonolysis or scCO<sub>2</sub> extraction were also suggested.<sup>164-166</sup> If it is not possible to assess univocally the overall sustainability of mesoporous materials processing, one can outline some interesting works where, in a conscious or unconscious way, some steps towards greener synthesis are proposed, although, to the best of our knowledge, no actual *all green* method to obtain a high quality mesostructured functional solids was ever reported.

Most studies on mesostructured silica have undoubtedly used TEOS as molecular silica precursor. Nevertheless, other interesting approaches exist. Galarneau *et al.* used pure SiO<sub>2</sub> spheres in presence of a cationic surfactant under hydrothermal conditions in a basic medium.<sup>167</sup> By this way, they could show that, probably through a dissolution-precipitation pseudomorphic mechanism, plain silica can actually be used without previous transformation. Boissière *et al.* showed that a structured material could be synthesized at neutral pH in presence of a PEO-based block copolymer if one starts from TEOS or sodium silicate.<sup>168</sup> When TEOS is used, a pre-hydrolysis step at pH= 2 under ambient conditions is required to hydrolyze and solubilize the alkoxysilane in water; then, the actual synthesis can occur at pH values between 4 and 8. As previously mentioned, ethylene glycol-modified silanes have been extensively used in the synthesis of mesostructured monoliths with hierarchical porosity in presence of non-ionic surfactants.<sup>56,169</sup> Three main reasons were given to support the higher sustainability of this approach: precursor is water-soluble, no alcohol is released and no catalyst is required.

## **6.2. Structure-directing agents**

The use of self-assembled surfactants as templates is the most common and easiest way to obtain a mesostructured metal oxide. So far, a large number of cationic, anionic and non-ionic surfactants have been successfully used.<sup>161</sup> Historically, alkylated quaternary ammonium salts were initially evaluated due to their similarity to ammonium salts used as molecular templates in zeolite synthesis.<sup>157</sup> To this regard, cetyltrimethylammonium bromide (CTAB) is by far the most exploited structuring agent to make mesoporous silica with pore size between 2 and 4 nm. In 1995, the group of Pinnavaia showed that non-ionic surfactants could actually be efficiently used to make mesoporous silicas.<sup>170</sup> Pluronics<sup>®</sup>, a series of polyethylene oxide (PEO)-polypropylene oxide (PPO) triblock copolymers, became an alternative to ionic templates for two main reasons: materials with larger pores (around 10 nm) and thicker walls (hence more stable) could be made and their richer phase diagrams opened the way to completely new three-dimensional mesophases.<sup>171</sup> Also very popular for their claimed low toxicity (see below), the Tween<sup>®</sup> surfactant series, that is non-ionic ethoxylated sorbitan esters, showed to be very efficient in the synthesis of both powders and films.<sup>172,173</sup>

At this stage, it is worth examining some features of most common surfactants used in mesostructured material synthesis (Table 2). In the context of this review, two main parameters must be addressed: biodegradation and toxicity. Biodegradation is the most important mechanism for the removal of chemicals from the terrestrial and aquatic environments by microbial organisms. The microbial organisms transform the contaminants through metabolic or enzymatic processes. The processes vary greatly, but frequently the final product of the degradation is CO<sub>2</sub> or CH<sub>4</sub>. Consequently, the evaluation of biodegradability is an indispensable element of the exposure assessment for the environmental risk evaluation process of a chemical substance.

Totally, there are three degradability statuses for surfactants to a given microorganism; (a) readily degradable, (b) hardly degradable, and (c) toxic.<sup>174</sup> These can be clarified by co-

degradation test of the surfactant with other carbon sources. Generally, biodegradation is a function of the nature of organic degrading microbial organism, the nature of the organic substrate, and the substrate-microbe interactions.<sup>175-178</sup> Surfactants, in general, have previously been appraised as being 'apparently' non-toxic to humans when present in concentrations of 1 ppm. However, more recent evidence strongly indicates the contrary for particular surfactants (Table 2).<sup>179</sup> The commonly recognized problems associated with the uncontrolled release of surfactants into the environment via watercourses and aquifers are manifold. It creates aesthetically undesired problem of foaming in rivers and drinking water (at levels below 1 ppm). The retention of surface-active properties can cause difficulties in wastewater treatment process. Moreover, the biological mineralization can severely increase the BOD (biological oxygen demand) in water bodies, with pernicious consequences. Herein lies a dilemma, on one hand, high levels of recalcitrance result in problems arising from the retention of surface activity, while rapid biodegradation of surfactants may seriously reduce the oxygen demand of the aquatic species.

Toxicity is the degree to which a substance is able to damage an exposed organism. Toxicity can be referred to as the effect on a whole organism such as an animal, bacterium, or a plant as well as effect on a substructure of the organism, such as a cell (cytotoxicity) or an organ (organotoxicity); e.g. liver (hepatotoxicity).<sup>180</sup> The word may be used to describe toxic effects on larger and more complex groups, such as the family or the society at large. More than ever before, there has been significant concern on the toxicity of surfactants or their breakdown products to living organisms. The discovery that nonylphenol is weakly estrogenic to mammals has raised concern regarding the environmental safety of major class of non-ionic surfactants, the alkylphenol polyethoxylates (APnEO, n= 6-40).<sup>181</sup> APnEOs are biodegraded initially via shortening of the hydrophilic chain, forming increasingly lipophilic

and persistent metabolites, including short chain alkylphenol ethoxylates and carboxylic acid derivatives and finally into alkylphenols such as nonyl- and octylphenol.<sup>181</sup> These metabolites are reported to be widely present in sewage, effluent, and river waters of Europe and the US, suggesting that the aquatic organisms are being exposed to the estrogenic chemicals. Other classes of surfactants such as sodium dodecyl sulfate (SDS; Table 2) and different sulfonates used in large quantities worldwide are also toxic to the environment.

The toxicological effects of surfactants, in general, is not possible to appreciate without understanding their physicochemical and biochemical properties. The strong protein-binding ability of certain surfactants is remarkable, where both ionic as well as van der Waals forces play a key role. The effect of SDS (sodium dodecyl sulfate) on muscle protein is such that it will cause changes in the viscosity and binding of alkyl sulfates to dermal keratin.<sup>182</sup> The inhibitory or stimulating effect of surfactants on enzymes can also be viewed in connection with their protein-binding capacity. Investigations on the effect of anionic surfactants on urease, pancreatolipase, and enolase were also been described. *In vitro* studies on keratinocyte gene expression in the presence of SDS showed an upregulation of involucrin (IVL) and downregulation of cytokeratin 1 (low weight, acidic type) expression, which is associated with the inflammatory epidermal phenotype found in psoriasis, and skin irritation. Cetyl trimethylammonium bromide (CTAB) treated skin showed more sign of cellular toxicity. The skin irritancy of most of the surfactants has been related to the inhibitory effect on saccharase.<sup>183,184</sup> Typically, the surfactants cause skin injury by several mechanisms that include direct cellular toxicity, disruption of barrier function, and surfactant specific effects on cellular differentiation.<sup>183,184</sup>

Strengthened biodegradation is one of the key means to treat surfactant pollution in the environment, and microorganism and the nature of the surfactant have significant effects on degradation. Zeng and co-workers have recently reported the co-degradation of cetyltrimethyl

ammonium bromide (CTAB) with glucose by *Pseudomonas aeruginosa*, *Bacillus subtilis* and composite microorganism in liquid culture media.<sup>175</sup> The result showed that CTAB was recalcitrant to degrade by the three microorganisms and it also inhibited the microorganism from utilizing the readily available carbon source. As shown in Fig. 5, in culture medium containing CTAB as co-degradation carbon source, the concentration of CTAB as well as TOC kept the initial high concentration unchanged, which shows that neither glucose nor CTAB could be utilized well by the selected strains. On the other hand, no growth of *Bacillus subtilis*, *Pseudomonas aeruginosa*, and the composite microorganism was observed in medium containing CTAB, showing CTAB's toxicity on the strains. The result strongly supported the anti-bacterial property of the cationic surfactant.<sup>175</sup> For instance, CTAB inhibited the growth of *Acinetobacter calcoaceticus* RAG-1 in liquid culture at very low concentrations and on agar plates at above 2  $\mu\text{g ml}^{-1}$ .<sup>185</sup>

The sub-acute and chronic toxicity of CTAB on rats was reported as early as in 1976.<sup>186</sup> High doses (45 mg/kg/day) of surfactants reduced the bodyweights of rats significantly. The food conversion was less efficient in male rats. However, no compound related gross pathologic changes were seen in autopsy and no microscopic alterations were found in the stomach wall and small intestine of the treated animal. Knops *et al.* have investigated the relationship between changes in physiological energetics of organisms and alterations of growth, development and reproduction of *Daphnia magna* under CTAB toxicant stress.<sup>187</sup> CTAB caused a reduction in body length of primiparous *daphnids* whereas a decrease in the reproductive performance was not apparent.

The discharge of chemical compounds into wastewater from hospital activities is a well-known problem, polluting water resources and constituting a serious ecological risk for the aquatic organisms. Glutaraldehyde (an alicyclic dialdehyde disinfectant) and surfactants (major component in detergents), are widely used in hospitals to eliminate pathogenic

organisms causing noscomial infectious disease. After use, disinfectants (GA) and surfactants (mainly CTAB, SDS, and TX) reach the wastewater network together. Studies were performed to investigate the combined acute toxicity effects of the toxicants on bacteria luminescence and *Daphnia* mobility at twice their CMC.<sup>188</sup> The mixture GA and CTAB was the most toxic followed by SDS and TX. Antagonistic interactions were observed for the joint action between GA and surfactants studied on *Daphnia*. This provides an outlook on the potential toxicity of certain hospital pollutants entering the aquatic environment and detected in surface and groundwaters.

There are no reports on the actual toxic effects of polymeric nonionic surfactants, Pluronic P-123 or F-127. However, BASF safety data sheets show the poor biodegradability of both the surfactants and acute and prolonged toxicity to aquatic invertebrates, plants, and other microorganisms (Table 2). Pluronics show gelation at body temperature at concentrations greater than 15 wt%. Such high concentrations led to notable toxicity and increased cholesterol and triglycerides levels in plasma after intraperitoneal injection in rats.<sup>189-191</sup> Pluronic F-127 has been reported to be the least toxic and therefore it has been the most widely used in drug delivery studies. Rill and Al-Sayah recently reported retardation of some peptides during the electrophoresis of oligopeptides, due to the hydrophobic effect of Pluronic F-127.<sup>192</sup>

The toxicological effects of Tween surfactants (ethoxylated derivatives of fatty esters of sorbitan; namely Tween 20, Tween 40, Tween 60, Tween 80 etc) are known from as early as 1977. Bresch and Ockenfels studied the influence of these surfactants on sea urchin embryo (*Sphaerechinus granularis*).<sup>193</sup> The results demonstrated that the development of sea urchin embryo is severely deranged by Tween surfactants. Toxic concentration rank is about

the same order as has been reported for similar nonionic surfactants. However, the toxicity concentration in sea urchin embryos is far below the concentration limits of toxicity in mammals. Arechbala and co-workers have made a comparative study of cytotoxicity of various surfactants including the Tween 60 and Tween 80 on normal human fibroblast cultures.<sup>194</sup> Accordingly the cytotoxicity of Tween 80 as determined by the MTT colorimetric assay ( $LC_{50} \pm SD$ ;  $\mu\text{g ml}^{-1}$ ) is  $210 \pm 15$ . Acute lung toxicity (respiratory distress) and intestinal damage of rats by Tween 80 surfactants have also been reported.<sup>195,196</sup>

Despite this accumulation of data on surfactant toxicity, very little effort has been done to improve the synthetic procedure from an environmental/health impact. A few examples exist that use natural, like phospholipids,<sup>197</sup> or biodegradable, like alkylglucosides,<sup>198</sup> surfactants. Clearly, this does not constitute a priority in the scientific community. Another explanation is that the surfactants are mainly used as sacrificial templates, mainly removed by calcination, *i.e.* with a limited amount of organic wastes.

### **6.3. Template removal**

As previously mentioned, removal of the structuring agent is also an important issue. At the moment, we are aware of two works that combine a good level of organization at the meso-scale without using any surfactant at all, and only in one single case an interesting strategy was conceived to remove and re-use the template under sustainable conditions. In both cases electrostatic interactions were preferred to weak van der Waals dispersion forces. Che *et al.* have used electrostatic interactions between fatty acids and an amino-modified silica. In this case, negatively charged carboxylate groups located at the external boundary of the micelle interact with positively charged amines belonging to the aminopropyl-modified silicon alkoxide.<sup>199</sup> However, elimination of the organic parts were performed by calcination and/or ethanol/water extraction steps. The work from Baccile *et al.* goes further.<sup>200</sup> Two water-

soluble (over the entire pH range) polymers are used in a complementary fashion: one is made out of a PEO block and a COOH-containing block (e.g., polyacrylic acid) and the other is an amino-containing synthetic polymer like polyethylene imine or even of natural origin like chitosan oligomers. In aqueous solution and in a particular pH range, positive and negative charges will coexist depending on the pKa of the components. Under these particular conditions, a micellar aggregate, referred to as a poly-ion complex micelle, is formed and can successfully template silica. Since the complex micelle is not formed by surfactants but by water-soluble co-assemblies, a change in pH will separate the two components that can be recovered and re-used as templates for further runs.

Some authors attempted to use biomass as templating agent disregarding the quality of the ordered structure. Wei et al. used, for instance, *D*-glucose, *D*-maltose or dibenzoyl-*L*-tartaric acid as porogens,<sup>201</sup> Polarz,<sup>202</sup> Yim<sup>203</sup> and Liu<sup>204</sup> used cyclodextrins (CD) while Schulz<sup>205</sup> used chitosan. In all cases but one, precursors were used as such, excluding additional structuring agents. The structure of final materials generally presents an amorphous mesophase but specific surface area values are fairly high, ranging from 400 to 800 m<sup>2</sup>/g for cyclodextrin and up to 1000 m<sup>2</sup>/g for *D*-glucose. In the case of Liu et al., CD were covalently attached to silica through urethane linkages between CD and an isocyanate-modified alkoxy silane. In all cases, the porogen was eliminated by a classical calcination step. One interesting exception is the formation of mesoporous silica materials using collagen as a porogen, where the templating biopolymer could be withdrawn using a proteolytic enzyme.<sup>76</sup>

## 7. Manufacturing

When speaking about “sol-gel”, the term “science” is often associated with the term “technology”. The main advantage of this synthetic route is to allow easy shaping of the final

oxide-based materials, and sol-gel process thus appears as an important liquid-phase manufacturing techniques among the so-called bottom-up approaches, for a large range of nanomaterials (particles, thin films, coatings, membranes, fibres or bulk materials). The literature is rather scarce regarding life-cycle assessment (LCA) of sol-gel derived products; however many researchers who have addressed life cycle aspects of nanoproducts, agree that the manufacturing phase is a major contributor to the life cycle impacts.<sup>206</sup> The authors would like to illustrate through selected publications, which are not restricted to the case study of silica, the current analysis that can be found on the environmental impacts of nanomanufacturing methods. Indeed many concerns have been raised regarding the human and ecological health effects of nanoproducts, but little attention has been given to the manufacturing phase. Top-down production methods are the most commonly used approaches today for nanoproducts, and it is generally believed that such techniques are more waste-producing than bottom-up techniques, that are often considered as the ultimate tools for sustainable manufacturing as they allow for the customized design of reactions and processes at the molecular level, thus minimizing unwanted waste.<sup>206</sup>

An interesting evaluation of a series of nanotechnological production methods (Chemical Vapour Deposition (CVD), Physical Vapour Deposition (PVD), flame-assisted deposition, sol-gel process, precipitation and lithography) was published.<sup>207</sup> Sol-gel process performed very satisfactorily in terms of facility installation cost, since it involves rather basic chemical process engineering (compared for example to lithography) and energy input (considered as low). The potential for release of nanoparticle emissions during the production stage was estimated low-to-medium regarding workplace since process takes place within liquid medium, but also low-to-medium regarding environment since discharge of nanomaterials is possible via polluted process media and wastewater. It is however noticed that discharge might be purified with adequate technology. During the product use, potential

for release of nanoparticles is low if nanoparticles are encapsulated in end-product within a fixed layer and medium if end-product shows no long-term stability.

In the course of the same study, life-cycle assessment (LCA) was also performed to describe the ecological efficiency potentials of nanotechnology-based coating processes.<sup>208</sup> The case study concerned corrosion protective coating on aluminium. Corrosion prevention has high economic as well as ecological relevance.<sup>209</sup> On aluminium, conventional coating technology requires the use of chromium, and chromium(VI) are known human carcinogens. A newly developed nanocoating based on sol-gel technology was compared to conventional coatings, such as waterborne, solventborne, and powder coat industrial coatings. In that case, the sol-gel coating was an organic-inorganic hybrid polymer, based on organosilanes. The assessment was carried out for the entire life cycle of the varnish, including surface pre-treatment: extraction of raw materials, production of basic components, varnish production, surface pre-treatment, varnishing, use stage application phase, disposal/recycling. The conclusion of this study was that sol-gel-based coatings show great potential for a very high degree of improvement of eco-efficiency with respect to all emissions and environmental effects (VOCs, greenhouse gases). It also allows a simplified surface pre-treatment process, avoiding chromating. Additionally, the same level of functionality can be reached for much lower thickness.

Sol-gel technology is also important for nanoparticle production for which exists a large offer of almost any composition at more and more competitive prices. But lower prices require more careful analysis of energy requirements in the possible process, and may enable both economically and ecologically safe choice of the required technology. An interesting confrontation was published<sup>210</sup> between liquid-based precipitation processes considered as traditional processes, and newer dry processes such as flame- or plasma assisted particle synthesis. Life cycle inventory was achieved using the emissions of CO<sub>2</sub> equivalents<sup>211</sup> and

energy balances as indicators. Emergence of new nanoparticulate materials repeatedly speculated that dry processes are more economic and environmentally friendlier than their wet counterparts due to fewer process steps. But indeed, in terms of energy requirement, product composition strongly influences the selection of the preferred method of manufacturing. The study focused on titania and zirconia nanoparticles. CO<sub>2</sub> emission for TiO<sub>2</sub> production was estimated to 4 kg/kg TiO<sub>2</sub> starting from titanium tetrachloride and to 15 kg/kg TiO<sub>2</sub> starting from titanium isopropoxide. For zirconia, these numbers are 5 and 9 respectively. The authors of this study concluded that what they called traditional wet processes based on salts (chlorides or sulfates) excel in terms of efficiency over dry processes based on organic precursors, especially for metal oxide nanoparticles of light elements with high valency. The purpose of this analysis was to compare energy consumption during nanoparticle production, indeed demonstrated the importance of the choice of precursors in terms of energy requirements.

Through those selected examples, it is clear that sustainable development of nanotechnology will inevitably require incorporation of life cycle thinking to analyze environmental impacts of nanomanufacturing.

## **8. Degradation and recycling**

If pure silica wastes are deposited in soils or in aquatic environments, dissolution will occur. It is usually considered that silica dissolution occurs via erosion, *i.e.* release of silicic acid from the material surface in direct contact with water.<sup>212</sup> The rate of silica dissolution depends on pH, temperature and humidity/rain events (weathering).<sup>213</sup> For instance, the dissolution rate increases by *ca.* 3 orders of magnitude when the pH increases from 4 to 10 and by more

than one order of magnitude when the temperature rises from 10°C to 35°C.<sup>214</sup> The presence of organic acids that can serve as ligands may also favor silica dissolution.<sup>215</sup> Besides these external factors, some of the intrinsic properties of the silica materials, such as porosity and particle size, influence its dissolution because this process starts from the material surface,<sup>34,216</sup> whereas the condensation degree appears a less significant parameter.<sup>217</sup> Besides these abiotic processes, the silica dissolution ability of some common living organisms (fungi, bacteria)<sup>218</sup> as well as of silicifying species (diatoms,<sup>219</sup> sponges<sup>120</sup>) was also demonstrated. The toxicity dissolved/degraded silica highly depends on its exact chemical form. Data on silica nanoparticle toxicity are not always consistent from one study to the other and strongly depend on the cellular model.<sup>220-222</sup> Once again, it is worth emphasizing that colloidal silica is very likely to be coated by bio-organic molecules present in the environment so that its reactivity can be very different from that of bare particles used in model experiments.<sup>216,222</sup> Examining molecular form of soluble silica, the toxicity of poly-silicic acids for human cells has been proposed to increase with the oligomerization degree.<sup>223</sup> However, due to the high concentrations of silica in soils and aquatic environments, it is considered that anthropogenic emission of SiO<sub>2</sub> contributes by few percents to the global silicon fluxes, and is therefore of limited environmental impact.<sup>37</sup>

Indeed the presence of metal ions within the silica network modifies the stability and therefore the degradation and/or dissolution kinetics of the inorganic network. Of primary importance is the environmental fate of microporous aluminosilicates due to their application in many processes including waste stream treatment, radioactive waste immobilization, and acid stimulation of petroleum reservoirs.<sup>224-227</sup> Early experimental observations by Murata established a general rule for zeolite dissolution and precipitation in HCl.<sup>228</sup> Those exhibiting a Si/Al framework ratio less than 1.5 dissolve subsequently, resulting in the formation of a gel, and those greater than 1.5 form a non-gel precipitate. The nature of dissolution,

stoichiometric or non- stoichiometric, was not evident as visual observations without any measurement of the aqueous silicon and aluminium concentrations were used as the basis of the general rule. Flippidis et al.,<sup>225</sup> observed that zeolites with low silica content were more reactive in distilled water than high silica zeolites. Further, Cizmek et al. reported the specific reaction rates of synthetic zeolites silicalite-1 and ZSM-5 decrease with decreasing Si-to-Al ratio in sodium hydroxide solutions.<sup>229</sup> These observations establish the framework Si/Al ratio of zeolites play a universal role in the dissolution mechanism independent of the framework type. Zeolites as such are considered not harmful in wet conditions and can be even used to reduce the environmental impact of heavy metals and organic molecules by adsorption.<sup>230,231</sup> However, after dissolution,  $Al^{3+}$  ions are released that can present strong toxicity, especially for plants.<sup>232</sup> Metallic species may also be present as nanoparticles doping the silica network. In this case, the degradation of the material is not expected to differ significantly from a pure silica phase but the released nanoparticles may exhibit their own intrinsic toxicity.

When Class I hybrid materials, *i.e.* when the interface between the organic and the inorganic components is based on weak interactions,<sup>233</sup> are concerned, then it is possible that the organic component degrades faster than the silica network. This is particularly true if this component is biodegradable since it becomes sensitive to biological activities. As recently demonstrated, this results in the fragmentation of the silica network and therefore enhances its solubility.<sup>39</sup>

To our knowledge, the environmental stability of Class II hybrid materials that involve a covalent bonding between silicon and an organic function has never been reported. However, the study of weathering effect on silicone polymers indicates that the Si-C bond is less sensitive to hydrolysis than Si-O-Si, but can be degraded by oxidation at moderately elevated temperatures.<sup>234</sup> Therefore, it can be assumed that the environmental degradation of

these materials can occur similarly to pure silica gels, except that organosilicates  $R_nSi(OH)_{4-n}$  are released during the dissolution process, that may present some toxicity.

Indeed, recycling must be envisioned as an alternative to waste production. Considering the re-use of pristine materials as such, industrial and consumer efforts have been made to recycle various forms of silica gel. When full transformation is required, two possibilities exist for pure silica gel: either dissolution in alkaline solution, similarly to silicones yielding back to aqueous silicates, either melting, as performed in the glass industry. When coming to hybrid materials, they can be treated as composite materials, involving pyrolysis or chemical treatments, to get rid of the organic matter.

As mentioned above, the influence of human activity on silica cycle is minor compared to the overall biogeochemical equilibrium of Si. A schematic overview of this cycle, where the impact of plant uptake and phytolith formation<sup>235</sup> have been discarded for sake of simplicity, is shown on Scheme 4. Silica can be extracted from white sand and used to generate aqueous silicates or silicon alkoxides via silicon production. Both precursors may be involved in the formation of silica-based materials. As a waste, silica can dissolve in soils and/or in open/underground waters and reach the oceans. There it is used by silicifying organisms, mainly diatoms, to form biogenic silica. After the death of these organisms, part of the shells will sediment and become integrated to white sand.<sup>236</sup>

## 9. Conclusions

A summary and critical evaluation of the above-described strategies that should help to make the sol-gel process “greener” is presented in Table 3. Looking back at the main categories classifying green chemistry principles (Scheme 1), it is clear that the three of them have been addressed in the field of sol-gel chemistry. However, in more details, the PROCESSING-ENERGY category may have been less explored. In particular P7-(Atom economy) and P11-

(Real-time monitoring) and process control have not been really discussed. In the first case, a survey of the literature indicates that sol-gel reaction yields are usually not mentioned. Indeed, in the case of silica gel, it is expected that all the silicon atoms are present in the final material. For alkoxides, there is a loss of C atoms due to hydrolysis step that is intrinsic to the process. For silicates, alkaline metals are usually incorporated in the silica gel but it may be necessary to remove them in order to enhance network condensation. Indeed, particle, thin films and hybrid material formation represents a different situation but the yield criteria does not appear to be a major concern, at least at the academic research level. In the second case, it is worth mentioning that many efforts have been made for the *in situ* investigation of sol-gel reactions, either directly (SAXS,<sup>237</sup> rheology,<sup>238</sup> DLS,<sup>239</sup> NMR<sup>240</sup>) or indirectly (fluorescent probes)<sup>241</sup>. However, these studies were mainly performed to get a better understanding of the gelation/structuration process.

In fact, it is worth noting that many of the alternative strategies described here were not explicitly developed to address sustainability issues, but because they give access to novel structures and/or functions. Thus, paraphrasing Molière's *Bourgeois Gentilhomme*, sol-gel chemists may have been “doing green chemistry without knowing it”. Paradoxically, when efforts were specifically made to improve the environmental integration of the silica sol-gel technology, benefits in terms of material properties were not always clear. This is very important because the « making » of a product is only one of the factors in the delicate balance that will determine the success of an eco-design approach. Indeed, the validation of these approaches implies a technological transfer from the laboratory scale to industrial production. At this time, silica sol-gel technology is mainly applied to the elaboration of powders, membranes, aerogels and thin films (coatings). For the first three examples, most of the proposed alternatives (silica source, precursors, solvents,...) may be evaluated whereas

the latter, that most of the time involve organically-modified silanes, should benefit from advances in processing techniques.

As mentioned earlier, no LCA analysis concerning silica sol-gel processes has been reported so far. In fact, although LCA for manufactured products containing SiO<sub>2</sub> such as tires are available,<sup>242</sup> it was reported that the lack of reliable data on silica recycling hinders a full analysis of the life cycle of such materials.<sup>243</sup> In addition, the environmental fate of silica was mainly studied for biogenic or geological SiO<sub>2</sub>, whereas data on synthetic silica are difficult to find in the literature.<sup>244</sup> This is also true for hybrid materials where the association of the two components may enhance (*i.e.* organic degradation favors silica dissolution) or slow down (*i.e.* the silica network decreases the accessibility to the organics) the dissolution process. To our point of view, this aspect constitutes a major direction of research for the full integration of eco-design in silica sol-gel chemistry.

Finally, as mentioned in the introduction section, sol-gel chemistry is indeed not limited to silica-based materials. Whereas most alternative strategies described above have already been applied to non-silica sol-gel reactions, some difficulties may arise due the different chemical reactivity of transition metal ions, especially towards water, when compared to silicon.<sup>14</sup> Moreover, from the perspective of renewable feed stocks, silica is unique in terms of availability, especially when biogenic forms are concerned. In parallel, silicic acid is considered as non-toxic and shows a low environmental impact, which is not the case for many metal ions. However, the history of sol-gel technology shows that concepts and processes initially developed in the frame of silica chemistry have always been adapted to other oxide materials.<sup>245</sup> Therefore, there is no reason to doubt that the “green revolution” will soon be extended to the whole domain of sol-gel chemistry.

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## Notes and References

†*Ethylene glycol, toxicity issues.* Systemic ethylene glycol toxicity can occur through ingestion since it is chemically broken down in the body into toxic compounds (e.g. oxalic acid). It and its toxic byproducts first affect the central nervous system (CNS), then the heart, and finally the kidneys. Ingestion of sufficient amounts can be fatal. Ethylene glycol is odourless and it does not provide any warning of inhalation exposure to hazardous concentrations. Breathing ethylene glycol vapors may cause eye and respiratory tract irritation but is unlikely to cause systemic toxicity. Ethylene glycol is poorly absorbed through the skin so systemic toxicity is unlikely. Eye exposure may lead to local adverse health effects but is unlikely to result in systemic toxicity.

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## Figure captions

**Fig 1** Relationship between eco-efficiency and ecodesign. Reprinted from ref 5, Copyright (2007), with permission from Elsevier.

**Table 1** E-factor measures for selected nanomaterial synthesis. Reproduced with permission from ref 8. Copyright 2008 Wiley-VCH.

**Scheme 1** Green chemistry principles and sol-gel chemistry. Adapted from refs 12 and 15.

**Scheme 2** Reaction path and end-products of silica reacting with ethylene glycol in strong basic medium. Reprinted with permission from ref 47. Copyright 1991 Nature Publishing Group.

**Fig. 2** (a) Silatranes obtained by Frye *et al.*<sup>48</sup> (b) Silatrane complexes obtained by Laine *et al.*<sup>49b</sup> Reproduced by permission of the Royal Society of Chemistry.

**Scheme 3** Representation of diol- and polyol-modified silanes used in silica-based sol-gel materials syntheses. Reprinted with permission from 59b. Copyright 2004 American Chemical Society.

**Fig. 3** Photographs of (a) silica aerogels obtained in scCO<sub>2</sub>, (b) IL-silica ionogels and (c) metal phthalocyanine-doped silica sonogels. (a)Reproduced with permission from ref. 110. Copyright 1997 American Chemical Society. (b) Reproduced with permission from ref. 91. Copyright 2006 American Chemical Society. (c) Courtesy O.G . Morales-Saavedra,CCADT-UNAM, Mexico<sup>141</sup>

**Fig. 4** Biocatalysis of silica formation : (a) activation of TEOS hydrolysis by the serine-histidine pair of sponge silicatein  $\alpha$ , (b) activation of silicate condensation by ammonium groups of diatom polyamines. Adapted from refs 123 and 126.

**Fig. 5.** Co-degradation of CTAB with glucose by *Pseudomonas aeruginosa*, *Bacillus subtilis* and composite microorganism in culture media. (○) Surfactant concentration in the culture medium, (●) TOC in the culture medium, and (▼) bacteria OD in the culture medium. Adapted with permission from reference 175. Copyright 2007 Springer Verlag..

**Scheme 4** (a) White sand can be industrially transformed into mineral precursors ('SiOH') (silicates, colloidal silica,..) or into silicon (Si) and organic (alkoxides) precursors ('SiOR') and converted into silica SiO<sub>2</sub>. (b) If deposited in the environment, silica is dissolved and transported by open air or underground water into the sea. (c) It is used by diatoms (≈) whose silicified structures form sediments that become part of the white sand