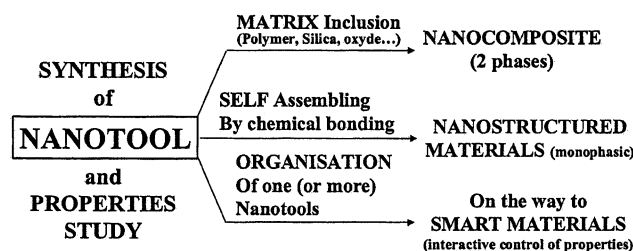# Organosilicon chemistry and nanoscience

Robert Corriu *

UMR 5637, Laboratoire de chimie moléculaire et Organisation du solide, Cc007, Université Montpellier II, Place Eugène Bataillon, 34 090 Montpellier France

Abstract

The BOTTOM-UP approach of nanosciences is a new field of research very broad in which the chemist is going to find many opportunities to create a wide range of new materials. The goal of nanosciences in the control of materials properties from the elemental scale (molecules, particles, clusters, etc.). The general scheme is giving a general overview of the different steps of BOTTOM-UP approach.

The aim of the paper is to comment on the different aspects and to stress the splendid opportunities that nanosciences are going to offer to organosilicon chemistry due to its great aptitude to design new solids and materials.
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Keywords: Nanosience; Nanomaterials; Organosilicon chemistry

1. Nanomaterials and nanosciences—generalities

1.1. Introduction

Nanosciences represent certainly one of the most promising developments for chemistry [1–3]. In this field the major challenge will be mainly the control of physical or chemical properties from the nanometric scale (atomic or molecular). This paper will emphasise the contribution of molecular chemistry and particularly organosilicon chemistry [4–7] in this very promising scientific domain.

1.2. What definition should we use for nanosciences?

From a chemical point of view a definition wide enough for nanosciences would be to consider them as all the ways of research focused on both nanotools and nanomaterials. The scientific aim is to design the properties (mainly physical and chemical, but possibly biological or mechanical) from the elemental scale (atoms, molecules, aggregates...). The synthesis and the study of nanotools enhanced with well defined properties as well as the discovery of assembly methods permitting the transformation of nanotools into nanomaterials are the core of the so called bottom-up approach of nanosciences. Chemistry has a very important place in this part of nanosciences, since it has now a very good control of the synthesis in every field concerned and since it has succeeded to find many

* Corresponding author. Tel.: +33-4-6714-3801; fax: +33-4-6714-3852.

E-mail address: corriu@univ-montp2.fr (R. Corriu).

routes for assembling molecules, particles, or in other words, nanotools.

Nanosciences correspond to both aspects, the design and the study of the properties of the nanomaterials, which can be obtained from nanotools. They are opening up a wide field of multidisciplinary research involving at least physicists for studies and chemists for designing. Let us explain more in detail the different steps.

1.3. Nanotools

These make up the elementary bricks of the future materials. They can be a molecule, an assembly of atoms such as a cluster, a metallic nanoparticle or the elementary stage of an inorganic combination (oxide, sulphide...). However, many of them will correspond to a specifically designed molecule for obtaining a desired physical: optical, magnetic, electric... or chemical: catalysis, selective separation... property, sometimes also a mechanical applications. In the near future, bio applications will certainly be developed. In all cases the property must be precise, able to be measured, and controlled. Nowadays the synthesis of the nanotool cannot be just a single chemical target. It must be mainly designed for reaching the property.

Moreover, it is also very important to stress the tuneability of the material. It must be in a way, that permits one to process films, matrixes or coating. A good example of that is all the research performed on the tuneability of ceramics such as SiC and Si_3N_4, which exhibit excellent thermo mechanical properties. Only the chemical way, starting from molecular organosilicon precursors transformed into polymers which are cross-linked afterwards (Fig. 1), permits one to obtain tuneable solids such as fibers, matrixes and coatings [8–14]. In this area, a one step preparation of a SiC coating was achieved from a single nanotool corresponding to a molecular precursor. The control of the viscosity was obtained by using a catalytic polymerization procedure. The tuneability of the crosslinked polycarbosilane was achieved by using a reversibly poisoned catalyst with a controlled oxidation [11–15] (Fig. 1). This is an example of the transformation of a nanotool into a tuneable material in one single step. In this case, the chemical interest of the molecule is very weak. Only the tuneability of the material and its practical utility are of interest.

The degree and the precision reached by chemical synthesis permits one now to prepare any chemical unit conceived around a property, whatever is the field of chemistry. Wide perspectives are thus open to the chemist. It is important to point out that some very simple molecules are potentially available to make up nanotools. One example is the case of the lanthanide complexes, which represent specific photoluminescent properties [16] (in the red for Eu^{3+} and in the infra red for Er^{3+}). Similar cases are the paramagnetic complexes obtained by coordination of Cu^{2+} in 1,4,8,11-tetraaza-cyclotetradecane (cyclam) [17] (schematically described in Fig. 2).

Metallic nanoparticles have also been developed [19]. However, more sophisticated systems have been also designed. One of the most illustrative examples is a molecular engine, which mimics the precise mechanical movements occurring on a molecular scale (Fig. 3) [1].

The principle of movement is based on the variations of the coordination stability of Cu^{1+} during the reversible redox process. In the reduced state, tetra coordination is the most favourable whereas after oxidation penta coordination is most stable, resulting in the creation of a new site of coordination due to the loss of the electron. The intramolecular movement allows the molecule to adopt the most stable configura-
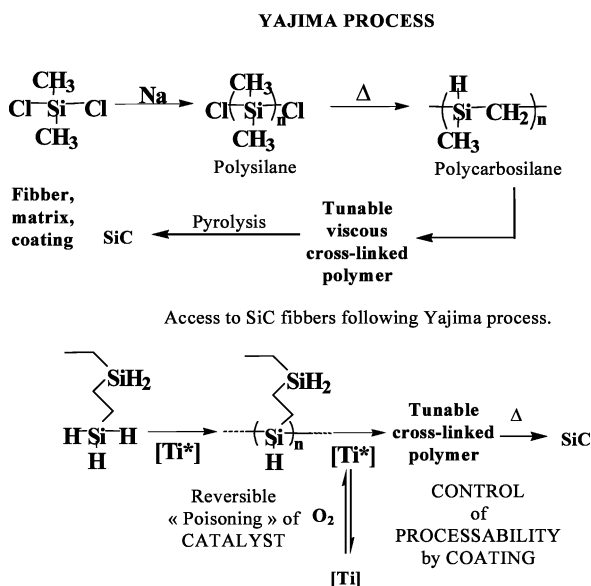
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Fig. 1. A one step catalytic preparation of SiC coating from a molecular precursor [15].
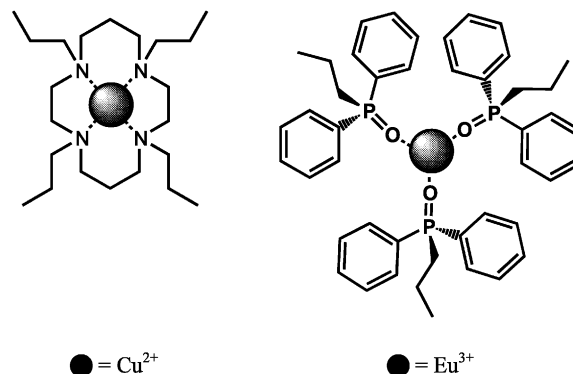

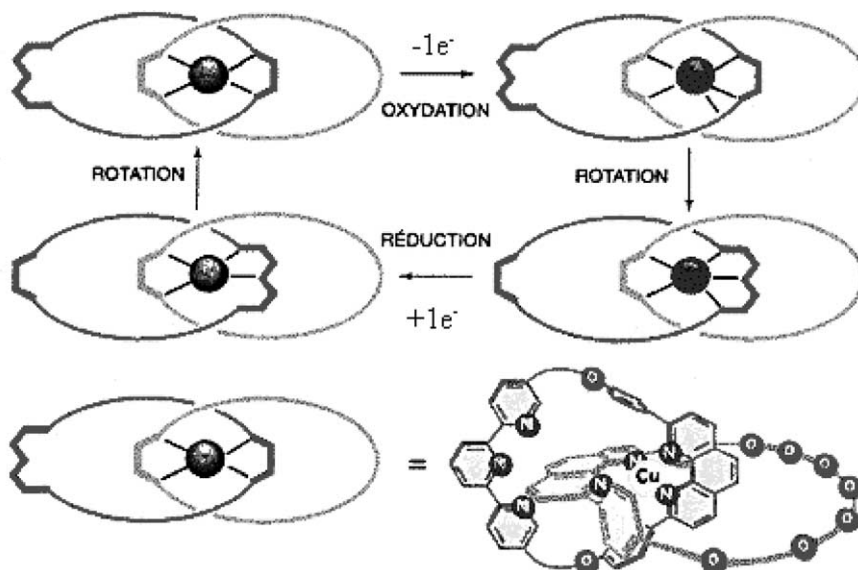Fig. 2. Simple nanotools designed for paramagnetism (Cu^{2+}) [18] and photoluminescence (Eu^{3+}) [16].

Fig. 3. of a redox driven molecular motion with catenan system

tion by passing from (2+2) to (2+3) coordination by oxidation and from (3+2) to (2+2) coordination by reduction. Thus, chemical stability is responsible for the rotation.

These two kinds of examples represent an illustration of the extreme possibilities. It is important to point out that the perspectives are extremely wide, from catalysis [20] (design of the catalytic site in the appropriate catalytic support) to physical devices for magnetic materials [21].

1.4. Nanomaterials by assembling nanotools

The synthesis and the study of nanotools enhanced with properties (physical or chemical) constitute the base to any research related to nanosciences. The study of the properties of nanotools [22] is a very important step for the knowledge of the possibilities that are open, taking into account the fact that the physical properties are highly dependant on the scale of observation, nanometric or micrometric.

It must, however, be pointed out that it is only a part of the target to reach nanomaterials and, in the long term, Smart materials. The isolated Nanotool is not a material: in the absence of an assembly and structure, it will remain a laboratory curiosity: nanotools are only a step on the way to nanomaterials.

Chemists have already discovered a large number of assembly methods and found effective organisation schemas for independent molecules. In the scope of nanoscience, this chemistry must be adapted and extended. It will be also important to explore new chemical ways for assembling nanotools in order to obtain nanomaterials corresponding to devices such as
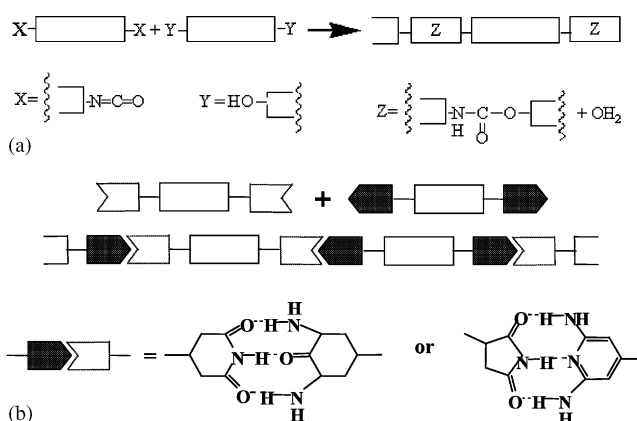

Fig. 4. (a) Example of assembling a single Nanotool by polyurethane formation. (b) Example of assembling a single Nanotool by supramolecular reaction.

coatings, fibers, matrixes or also solids with a controlled porosity.

1.5. General methods for access to nanomaterials: nanocomposites versus nanostructured materials

Nanocomposites [23,24] are obtained by inclusion of nanotools in a matrix. This matrix can be an organic polymer or an inorganic matrix, the most popular in the latter case being silica. In such composites, the material is biphasic since by simple extraction procedures of washing, it is possible to separate the nanotool from the matrix (organic or inorganic). However, it must be pointed out that this is a very convenient way to obtain nanomaterials focused on one well-defined property.

This is, and it will be, a more and more popular approach to nanomaterials.

Nanostructured materials [25]. These are obtained by assembling the nanotools by using chemical bonding. In such a case, the solids obtained are monophasic since the nanotool cannot be separated from the organic (polymer) or inorganic matrix. These materials will be called nanostructured by distinction from nanocomposites.

Two ways can be used for assembling such materials: organic or inorganic polymerization. In both cases the nanotool must be chemically designed in order to permit the formation of a matrix around it by chemical bonding. These possible general ways involve organic or supramolecular polymerization or inorganic polycondensation (sol–gel type chemistry).

1.5.1. Organic polymerization

The general assembly of a nanotool is represented simply here, as an example, in the form of a linear assembly (Fig. 4). The nanotool must be functionalised for polymerization. The scope of polymerization possibilities is extremely wide: polyesters, polyamides, polyolefins... Fig. 4 illustrates the assembling method of a single nanotool by polyurethane polymerization. It is also important to point out that supamolecular chemistry is also a possible way for assembling nanotools, either by hydrogen bonding [26] or by controlled coordination chemistry [27]. Fig. 4 also illustrates the possible use of hydrogen bonding for nanomaterial preparation.

1.5.2. Inorganic polycondensation (a sol–gel type process)

These methods are well known since the discovery of the sol–gel process, due to Ebelman in 1848. It is important to point out that this purely mineral synthesis is the sister of the organic polymerization. This hydrolytic polycondensation reaction of a Si–OR bond corresponds to a nucleophilic substitution of the oxygen atom either of H_2O or a Si–OH bond on the metallic center of another molecule. This reaction leads to the formation of Si–O–Si bonds, the propagation of which results in oxide [28] formation by a kinetically controlled process [29]. Fig. 5. represents the details of the different stages leading to silica [30] starting from the hydrolysis of $Si(OR)_4$.

This way is a very convenient one for the preparation of nanomaterials since in one step it is possible to obtain the solid by passing through the tuneable colloidal sol (step 3), which opens the possibility to perform coatings and to obtain a fiber or a matrix.

This research field will be more developed in the following section since it represents a very efficient and very powerful tool for the chemist, making the material science compatible with many different aspects of chemistry that initially were separated: solid state chemistry, organic and inorganic chemistry, organometallic and coordination chemistry, macromolecular chemistry and also biochemical aspects. The terminology 'chimie douce' [31] was introduced to emphasize the contrast with the usual method of solid-state chemistry requiring high temperature processes [32,33]. The materials prepared by the classical high temperature method are thermodynamically controlled materials. In contrast, the inorganic polymerization (sol–gel type process) leads to kinetically controlled solids [31]. These two ways do not give the same results. Thus, the route illustrated in Fig. 5, and readily extended to other solids than SiO_2 is not in competition with the classical thermal routes used in solid state chemistry: it corresponds to a molecular way for material science, leading to different kind of materials.
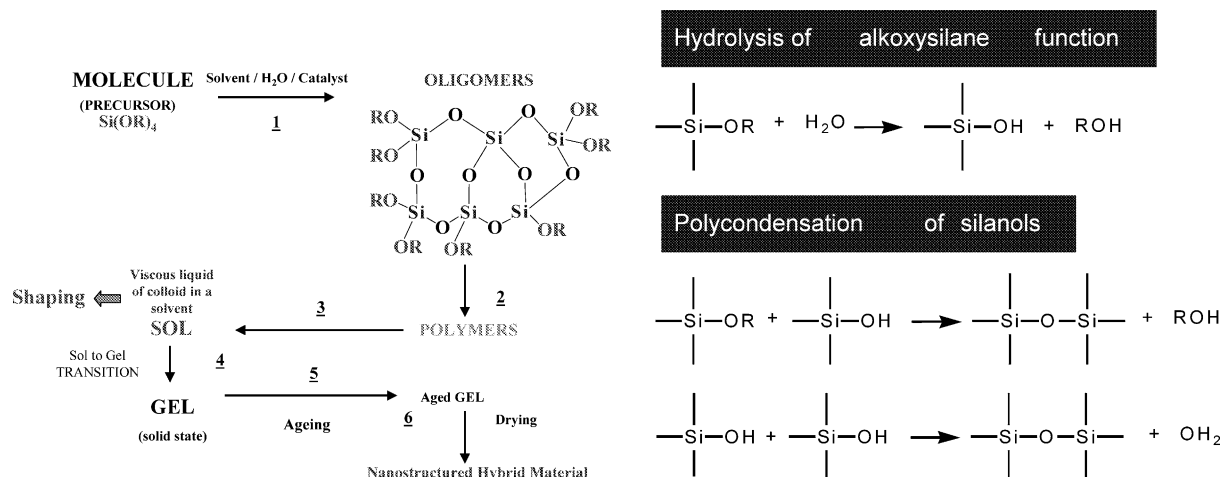

Fig. 5. Chimie Douce [32]: inorganic polymerization of silica precursors

2. Nanomaterials and sol−gel process

2.1. Silicon, the 'ideal' element for hybrid materials chemistry and nanosciences

Compared to other elements, silicon appears as the most convenient and fruitful element for the preparation of monomers required for the design and preparation of new materials. In fact, the number of elements, which permits the maintainance of covalent metal–carbon bonds under hydrolytic conditions is very limited. For instance, transition metal and Group III elements cannot be used because of the high reactivity of the metal carbon bond towards H_2O. There are possibilities with elements of Groups IV and V. However, taking into account other requirements, it is obvious that only P and Si exhibit a reactivity and stability fully compatible with the preparation of hybrid materials. The chemistry of organogermanes is difficult and expensive, derivatives of arsenic are toxic, and stability of organotin and a fortiori organolead compounds is limited. However, it will be certainly possible to develop some interesting devices and materials with some of these elements, particularly in the case of Sn and B.

There are many reasons for the unique character of silicon:

a) Organosilicon chemistry has reached a high level of development and its fundamental rules are now well understood [34].
b) The characterisation of solids at the molecular level is also well established by several techniques [3].
c) The conditions required for the formation of the inorganic network are mild, and almost all the types of Si–C bonds survive them: $Si–C_{sp^3}$ is very stable, $Si–C_{sp^2}$ can be cleaved under severe conditions, $Si–C_{sp}$ is also stable but it can be easily cleaved under very specific conditions [3].
d) Many different leaving groups can be used for the formation of the Si–O–Si inorganic network (OR, H, Cl,...) [35].

e) The qualities of the Si–O–Si network are excellent in terms of thermal and chemical stability.
f) The Si–O–Si matrix is easily accessible to many reagents, whatever the specific surface area and porosity of the solid.
g) The Si–O–Si matrix also exhibits a very good transparency, which is very convenient for optical devices.
h) However, the most interesting feature is the great compatibility of silicon with many aspects of chemistry. A silicon unit can be introduced in almost all types organic or inorganic of chemical structures [36]. In the scope of materials chemistry and particularly in the nanoscience approach, silicon will permit to building up of a solid matrix around the nanotool by using the binding of hydrolysable SiX_3 groups on the nanotool, as is illustrated in Fig. 6.

2.2. The main Silylation routes for nanotools

The hydrosilylation reaction is one of the most convenient method for introduction of $–Si(OR)_3$ or $–SiCl_3$ groups on a molecule by using a well know catalytic process [37]. The Calas–Dunogues reaction and Grignard reaction between aryl halogenide and chloroalkoxysilane are other examples that allow a direct grafting of $–Si(OR)_3$ to aromatic units [38]. An alternative route consists of the formation of a lithiated compound, followed by silylation with chlorotrialkoxysilane. Some new Grignard reagents like $ClMg–CH_2–Si(O^iPr)_3$ [39] or $BrMg–C_6H_4–Si(O^iPr)_3$ [40] are interesting synthetic tools. Another general route is the Benkeser reaction that allows efficient preparation of precursors with the allyl or benzyl group [41]. As a last example, the Heck type reaction (or some modification) is certainly one of the most powerful tools that can be used in the preparation of precursors since this reaction can be performed directly with synthon bearing $–Si(OR)_3$ substituents [42]. The introduction of the $CH_2=CH–Si(OR)_3$ group is easy by this way [43]. Very recently, a very convenient catalytic method for the substitution of aryl bromide by the $Si(OR)_3$ group [44] has been reported.

2.3. Nanostuctured hybrid materials, a first step to nanosciences

The synthetic methods described above are of very great interest for the preparation of nanomaterials. They correspond to very useful ways, which permit the transformation of the nanotool into a nanomaterial. In one single step, it is possible to obtain the solid material, thanks to the sol–gel process. Some examples are summarised in Fig. 7. They illustrate the very rich potentiality opened up by organosilicon
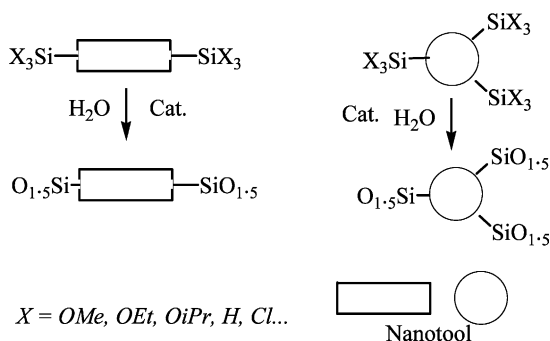

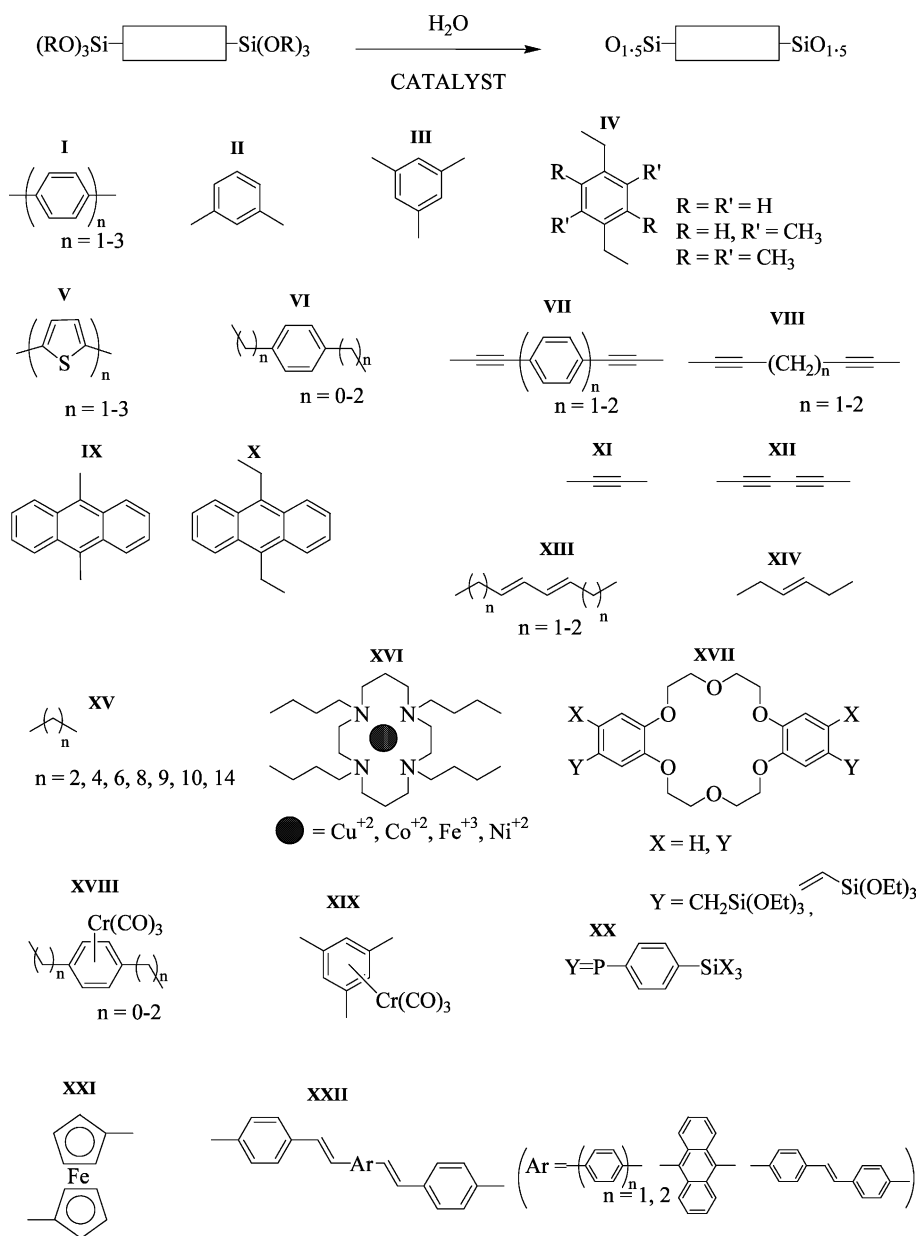Fig. 6. scheme of building up a silica matrix around a nanotool

Fig. 7. Some examples of bridged polysilsesquioxane monomers.

chemistry from the perspective of assembling Nanotools. In all cases, the organic unit is maintained in the solid without any change and the solid exhibits the physical property of the organic unit.

Many hybrid materials have been prepared by this way. Only those, which exhibit physical or chemical properties, correspond to nanomaterials. There is for instance the case of those containing metallic centres [XVI [45] (optic, magnetism), XVIII, XIX [46], XXI [47] (electrochemistry) or organic units with particular physical properties [V] [48,49](electrochemistry), XXII [50] (photoluminescence)].

2.4. Nanoporous materials[1]: on the way to Smart materials

Smart materials are one of the main challenges for nanosciences. They correspond to nanomaterials in which at least two physical properties will be interactively coupled together. Until now the chemistry, which could permit the access to such materials, is not known.

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[1] The terminology 'mesoporous material' does not describe precisely these materials in which the mean pore size is in between 2 and 50 nm. The terminology 'nanoporous materials' is rather precise and now more and more used.

Some ideas are under investigation and one of the most exciting ways involves the use of nanoporous materials.

The discovery of MCM-41 materials [51,52], which exhibit large specific surface areas and narrow pore size distributions has opened very wide perspectives for chemistry, since they are potential candidates for a variety of applications in chemistry (catalysis [53] and separations for instance [54,55]) but also for physical properties (optic, magnetism, electric conductivity...). These solids are also a very nice opportunity for organosilicon chemistry. Until now, silica is the most convenient matrix in which these materials are studied and developed. Thus organosilicon chemistry is the unavoidable route for their preparation.

The nanoporous materials are obtained by a sol–gel type polycondensation performed in the presence of surfactants (Fig. 8). This procedure leads to the formation of solids in which channels have been designed by a surfactant working as a template. After elimination, in most of the cases, the materials obtained exhibit a very regular hexagonal packing distribution of the pores in the silica matrix. Moreover, recent results obtained on films prepared by dip coating, indicate that one can obtain, in most cases, pores of highly regular size with a hexagonal morphology [56].

The inclusion of functionalities precisely located in the pores can be performed either by grafting of an organosilicon compound such as (A) after elimination of the surfactant template [57–61] or by direct synthesis (cf. Fig. 9) [62–74]. In this last case, the spacer of (A) must exhibit lipophilic properties, compatible with the core of the micelle. This route provides a more regular distribution of organic groups inside the channel pores than by grafting and allows the control of the organic content.

These materials are of great interest for nanosciences. For the first time, chemists are faced with a single material, which exhibits all together the three aspects of chemistry: chemistry in the solid (bulk of the nanoporous material) chemistry in solution (channels) and chemistry at the surface (functionalisation of channels). Thus, the next goal for chemistry is to find ways of permitting the control of functionalisation in the bulk but also in both the channels and on the surface of the pores. This last possibility is a very interesting one since the surface of the nanoporous material is very high

(sometimes higher than 1000 m^2g^{-1}). That enables the linkage at the surface of an amount of functionalities sufficient for an easy characterization using directly classical methods (solid state NMR, IR, etc.). This represent a very interesting enhancement of the available possibilities for characterisation on a simple planar surface by indirect methods.

In order to illustrate the easy characterisation, let us present some recently published results, in which the possibility of using ^{31}P-NMR spectroscopy permits a very precise determination of the distribution of phosphines in the channels. The materials have been prepared by using the direct synthesis methodology including as precursor (A) $(MeO)_3Si-(CH_2)_3PPh_2$ in the micelle [72]. It is possible to measure the distribution of phosphines linked along the channels by changing the ratio A/TEOS. ^{31}P-NMR spectroscopy permits us to achieve this measure by using the reactivity at phosphorus of p-dibromoxylene, which can bridge two P atoms in a close proximity (Fig. 10). In another example, the complexation of Eu^{3+} was considered after oxidation of the phosphine [73]. This complexation occurs in the ratio of 3 $\equiv$P=O centers for one Eu^{3+} (Fig. 10).

These results illustrate very well the regular distribution obtained in the pores by the inclusion of the functionalities in the channels.

The potentialities open by the possible functionalisation of the pores by using precursors like (A) are very wide. It permits the introduction of much more than one simple chemical function. For instance some photoluminescent ions (Eu^{3+}) and some metallic nanoparticles have been already grafted in to the pores as well as a few paramagnetic species like (Cu^{+2}, Co^{+2}...) [45].

Finally, it must be mentioned that recent developments in this field concern the preparation of nanoporous materials prepared from precursors such as those described in Fig. 6. Inagaki et al. [75] Stein and co-workers [76] and Ozin and co-workers [77–79] succeeded to obtain nanoporous materials from bis silylated precursors where the organic groups are located in the bulk. These new materials exhibit hexagonal organization of the pores and provide the possibility to include chemical groups in them. Moreover, recently for one of these materials called periodically mesoporous organosilica (PMOS), a very nice organization has been shown [80].
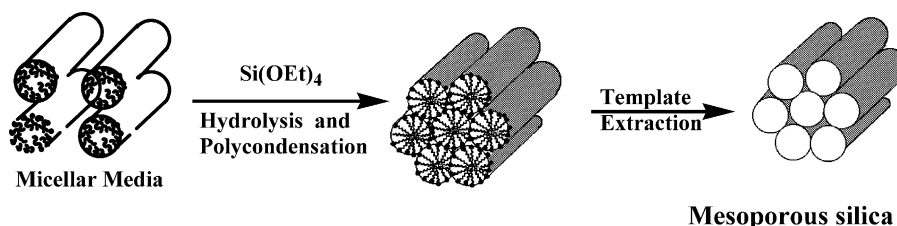
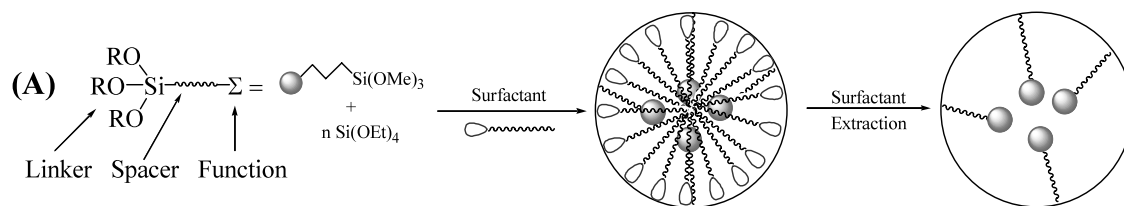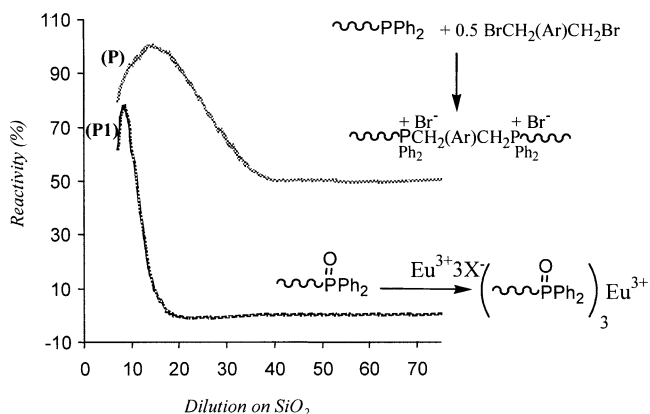Fig. 8. Schematic pathway for MCM-41 formation.

Fig. 9. Direct synthesis of a hybrid material in the presence of surfactant.

Fig. 10. Reactivity of grafted phosphino groups as a function of the ratio phosphino group/SiO_2. (P) Diphenyl phosphino group with bridging *p*-dibromoxylene. (P1) Diphenyl phosphino oxide acting as the chelating group for Eu^{3+}.

By extending this methodology to the case of chelating units, we have obtained materials including tetra-azamacrocyles in both the framework and the channels [45] (cf. Fig. 11). The coordination chemistry of these solids has been achieved. It was possible to include Cu^{+2} and Co^{+2} in both the framework and in the channels with absolute control of all the possibilities: only in the pores, only in the framework, a single ion in both channels and bulk, and also one ion in the pores and another in the framework and vice versa.

This example illustrates very well that chemistry can be adapted in order to obtain the control of the location at the same time in the bulk and in the channels. The introduction of ions corresponds to the potential inclusion of a physical property. The extension of this work permits the incorporational Eu^{3+} (photoluminescence) and Gd^{+3} (luminescence and magnetism) in the frame-
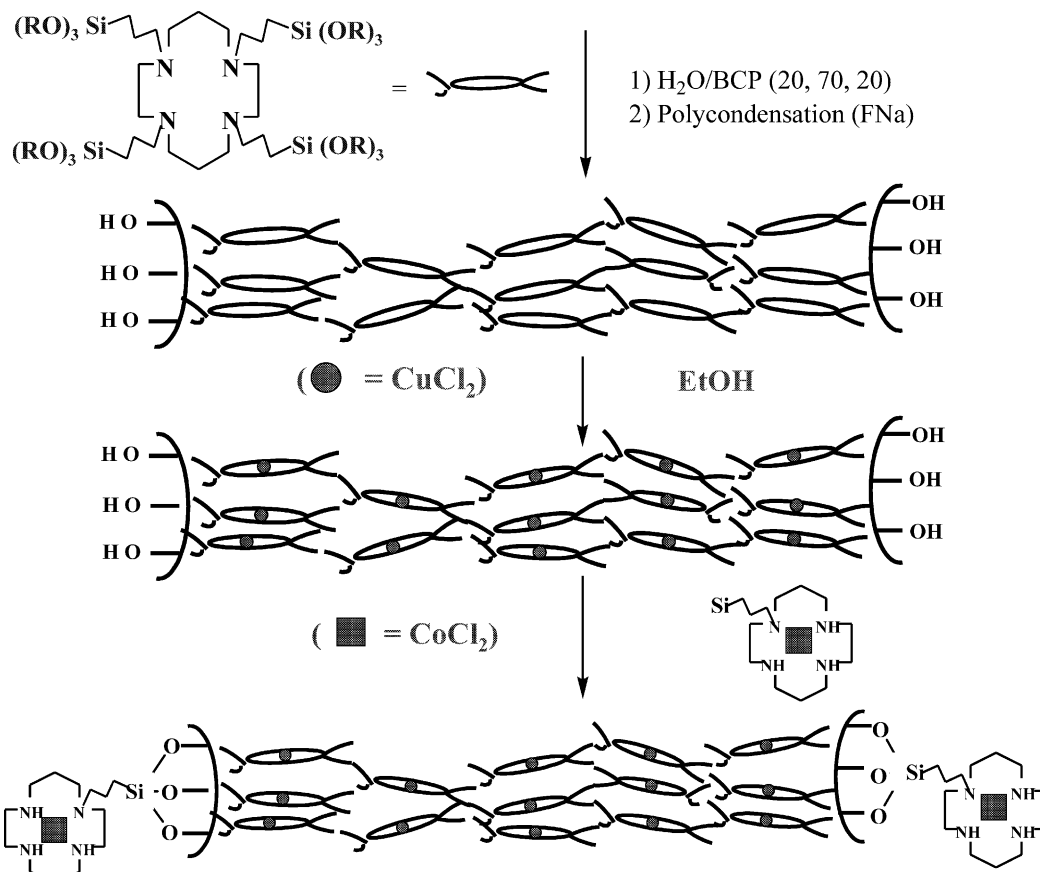
Fig. 11. Mesoporous hybrid materials containing chelated Co^{2+} in the channel pores and Cu^{2+} in the framework.

work, while other ions like Cu^{+2}, Co^{+2}, Fe^{+3} and Ni^{+2} are included in the pores [81].

These examples illustrate the wide possibilities that are open for these kind of materials in the field of nanomaterials.

3. Conclusion

The aim of this paper was to show the possibilities open for nanosciences in the field of organometallic chemistry both for transition and organoelements (representative elements).

There is a very wide scope available for the chemical control of the physical properties. The few examples given illustrate very well that the main limitation for building up new materials is in finding new chemical routes. Thus, the chemists will have to play a very important role in the development of nanosciences and organosilicon chemistry will be one of the favorite tools for designing materials and devices.

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