New materials by sol–gel processing: design at the molecular level

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The creation of powerful new materials for innovative applications is one of the big scientific and technical challenges of our days. This challenge can only be met by a multidisciplinary approach, in which, however, preparative chemistry plays a fundamental role. It provides the compounds which eventually will be shaped into new devices by materials scientists and engineers. The design of the macroscopic properties of a material by the deliberate selection and tailoring of nanoscopic building blocks is a new approach in inorganic chemistry, although it has a long tradition in macromolecular organic chemistry.

One of the modern methods for preparing inorganic materials from molecular precursors is the sol–gel process.[1] It not only allows the preparation of known materials in a new way (often combined with physical or technological advantages), but also materials with novel compositions and properties. The aspect of 'designing' inorganic materials (or material properties) is becoming a realistic possibility.

The sol–gel approach to material syntheses is based on hydrolysable molecular precursors, mostly metal or semi-metal alkoxides. Hydrolysis and polycondensation reactions lead to the formation of oxo polymers or metal oxides. These fundamental chemical processes are influenced by several parameters which, once they are understood for a particular chemical system, allow the control of the homogeneity (or controlled heterogeneity) and the nano- and micro-structure of the derived material.

'Design' of sol–gel materials therefore is possible, in a simplified sense, by variation of the chemical composition of the molecular building blocks and by variation of the nano- and micro-structure. Both influence the properties of the final material to a very high degree. The following examples are mainly taken from my own work, because this article is intended to be a personal account rather than a comprehensive review on the subject. By doing so one should not disregard the seminal contributions and fundamental work of other groups.

Design by Variation of the Chemical Composition

There are two possibilities to modify the chemical composition of sol–gel materials: by using precursor mixtures and by chemical modification of the precursors.

Many oxide ceramic materials consisting of more than one metallic or semi-metallic element were prepared as powders, green bodies, fibres, coatings, *etc.*, by sol–gel processing, starting from mixtures of hydrolysable molecular compounds (alkoxides, carboxylates, *etc.*). When oxide ceramics are made in the classical way from single oxides by solid-state reactions ions have to diffuse through crystal lattices. Activation energies, and thus the temperatures necessary to get crystalline phases, usually are much lower when the ceramic material is formed from an (amorphous) gel with a high dispersion of the individual components.

The kind and ratio of the different elements in ceramic materials is of course predetermined by the composition of the crystalline phase. However, dense, non-crystalline materials with interesting applications (mainly as coatings) were also developed by sol–gel processing, and their properties largely depend on their chemical composition. The classical approach to combine the properties of different materials led to the development of composite materials or blends, where different macroscopic phases with complementary physical properties are combined. The concept of composites originated in the idea of producing a material having better properties than those of either of the two components. The chemical equivalent to composite materials is the combination of different chemical groupings (with different properties) on a molecular level in one macroscopically homogeneous material.

Among the sol–gel materials developed by this approach, those composed of both organic and inorganic components (organic–inorganic hybrid materials) are particularly useful, because of the very different properties of the components being blended. The possibility of incorporating organic moieties arises from the low reaction temperatures during sol–gel processing.

Hybrid materials with different combinations of properties are obtained by variation of the kind and ratio of organic and inorganic groupings, and by the way that these are connected.[2] There are two principal possibilities. (1) Organic molecules or polymers are embedded in an inorganic matrix. These materials are synthesized by carrying out the hydrolysis and condensation of the inorganic compound, *i.e.* the formation of the inorganic matrix by sol–gel processing, in the presence of the organic compound. (2) The inorganic and organic components are connected by covalent bonds. This approach requires molecular precursors that contain a hydrolytically stable chemical bond between the element that will form the inorganic network during sol–gel processing and the organic moieties.

The advantage of the first type of hybrid materials is that no extensive modification of the starting compounds, *i.e.* no particular 'precursor chemistry', is necessary. Various organic–inorganic hybrid polymers with interpenetrating (but not connected) organic and inorganic networks have been prepared, and organic molecules of different kinds (dyes, catalysts, enzymes) were entrapped in the inorganic host matrix without losing their chemical properties.

The key for the development of hybrid materials of the second type is a suitable molecular precursor of the general type $Y_nE–X–A$, where Y_nE is the hydrolysable moiety forming the inorganic structure during sol–gel processing, A is a (functional) organic group, and X is a chemically inert spacer permanently linking E and A. The grouping Y_nE is a metal or semi-metal alkoxide moiety (Y = OR) in most cases. The chemistry and applications of organofunctional alkoxides were recently reviewed.[3] The group A can be nearly any organic or inorganic group if it is hydrolytically stable. It may serve several purposes, such as modifying the network structure, introducing organic functionalities into the inorganic networks, or providing reactive groups for organic cross-linking reactions.

Most hybrid materials of the second type developed so far are silicate systems. The reason is the hydrolytic stability of Si–C bonds, which allows an easy anchoring of functional organic groups. A variety of precursors of the type $(RO)_3Si{-}X{-}A$ is commercially available or can easily be prepared. The spacer X is a $(CH_2)_n$ chain in most cases. Hydrolysis and condensation of such precursors results in the formation of compounds of the type $O_{1.5}$ Si–X–A, in which the functional organic groups A are bonded to the polysiloxane network *via* the spacer X. The materials can be inorganically 'diluted' by cohydrolysis of $(RO)_3Si{-}X{-}A$ with $Si(OR)_4$ in any ratio. The higher the amount of the latter in the starting mixture, the lower is the concentration of the organic groups in the final material. It should be pointed out, however, that sol–gel processing of mixtures of different alkoxides requires careful elaboration of the reaction conditions to avoid uncontrolled phase separations or to obtain a defined distribution of the different building blocks (see below).

When $Si(OR)_4$ is successively replaced by $(RO)_3Si{-}R'$ the average degree of cross-linking per silicon atom drops from 4 to 3, *i.e.* the cross-linking density is lowered (in reality the degree of cross-linking is somewhat smaller, due to residual Si–OR and Si–OH groups in the final materials). Lowering the cross-linking density results in a modification of the microstructure and the mechanical properties. If this is the only goal of the system modification, simple organic groups, such as alkyl or phenyl, can be used as the substituents R′. It should be kept in mind, however, that lowering the cross-linking density is an inevitable side-effect, when organic groups are introduced for other purposes. For some applications it therefore may be necessary to balance the $(RO)_3Si{-}X{-}A : Si(OR)_4$ ratio carefully (an example is given below).

The introduction of organo*functional* groups, *i.e.* the use of alkoxysilanes of the type $(RO)_3Si{-}X{-}A$, results in a more extensive chemical modification of the materials. The properties of the organic functions A supplement those of the polysiloxane matrix formed by hydrolysis and condensation of the $(RO)_3Si$ and $(RO)_4Si$ units. Most work has been done with silanes, in which the functional group A is a chromophore (mostly non-linear optical chromophores), a metal complex entity (mostly for heterogenizing homogeneous metal catalysts [4]) or a group capable of forming organic polymer units. Examples of such compounds and their applications are given elsewhere.[3]

Compounds in which A is a polymerizable group allow the preparation of inorganic–organic copolymers, which constitute the technically most advanced type of applications for hybrid materials, mainly as coatings. In most examples the precursors $(RO)_3Si{-}X{-}A$ are first treated with water. After sol–gel processing, the organic groups A attached to the inorganic building blocks are thermally or photochemically polymerized or cross-linked to form the organic structures.

Another approach is to reverse the order of formation of both networks. For this purpose, compounds of the type $[(RO)_3Si]_xY$ are used, in which Y is an organic group or a macromolecule linking two or more $(RO)_3Si$ units. The structure of the preformed organic building block Y is retained in the final material. The organic substructures are cross-linked by hydrolysis and condensation of the $(RO)_3Si$ units, *i.e.* by formation of the inorganic network.

The copolymers obtained by either approach consist of dual polymer networks, in which cluster- or polymer-type inorganic structures are linked by organic groups or polymer fragments. What makes these materials unique is that they combine to some extent the properties of organic polymers with those of metal oxides. In general, the physical properties of the copolymers are between those of purely inorganic and purely organic polymers, with the option to shift them gradually from one extreme to the other by changing the ratio of the organic and inorganic building blocks. Although the properties of the inorganic and organic units are of course not strictly additive with regard to those of the resulting copolymer, the general concept is sound.

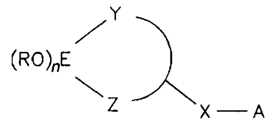
The hydrolytic stability of Si–C bonds allows an easy anchoring of the functional organic groups. Contrary to this, bonds between carbon and metallic elements are cleaved by water. Therefore, the precursors $(RO)_nE{-}X{-}A$ for organically modified *non-silicate* systems must contain other groups X of sufficient hydrolytic stability to link $E(OR)_n$ and A. Suitable groups are anionic chelating (**I**) or bridging ligands.

The reactivity of metal alkoxides towards water is much higher than that of alkoxysilanes. While catalysts are needed to enhance reaction of the latter, chemical additives (mainly acetic acid or acetylacetone) are used to moderate the reactivity of metal alkoxides. When non-silicon alkoxides $E(OR)_y$* are treated with carboxylic acids, for example, part of the alkoxide groups is substituted by (mostly chelating or bridging) carboxylate groups. A new molecular precursor $E(OR)_{y-x}(O_2CR')_x$ is formed which exhibits a different reactivity. Upon addition of water, the alkoxy groups and not the complexing ligands are primarily hydrolysed,[5] and materials of the idealized composition $EO_{(y-x)/2}(O_2CR')_x$ are obtained. The role of the carboxylate group in the new precursor $E(OR)_{y-x}(O_2CR')_x$ is similar to that of the organic groups R′ in $(RO)_{4-x}SiR'_x$: they block condensation sites, lower the degree of cross-linking in the oxide materials and introduce organic groups R′ into the sol–gel materials.

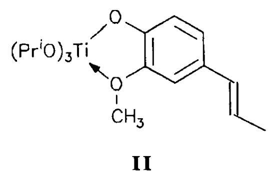
Contrary to the silicate systems, one has to consider the long-term stability of the link between the oxide-forming element and the organic groups. For example, the hydrolysis rate of a $Ti(O_2CR)$ group is much lower than that of a Ti(OR) group, *i.e.* the carboxylate groups are retained during sol–gel processing to a sufficiently high degree. However, under more forcing conditions or upon extended exposure to moisture the carboxylate groups may also be cleaved.

It is well known in co-ordination chemistry that the formation of five- or six-membered metallacycles by chelating ligands results in considerable stabilization of the metal–ligand bond. For example, the Ti–O bond of the isoeugenolate ligand in **II**, prepared by reaction of $Ti(OPr^i)_4$ with isoeugenol, is much stronger than that of the OPr groups. This is due to chelation by the α-methoxy group. The OPr groups were cleaved during base-catalysed hydrolysis, while one isoeugenolate ligand per two titanium atoms was retained.[6]

Strengthening of a metal–ligand bond by the chelate effect is also a good strategy for carboxylic acids. This was recently shown for α-amino acids. The structure of $[\{Ti(OEt)_3(GlyO)\}_2]$ (GlyO = glycinate) was determined by an X-ray diffraction analysis, **III**. Owing to the formation of a five-membered chelate ring by co-ordination of one oxygen of the carboxyl group and the α-amino group, the hydrolytic stability of the aminocarboxylate derivative is much higher than that of the corresponding derivatives with simple carboxylic ligands.[7]



I



II

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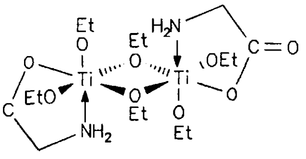
* Only monomeric formulae are used in this article for simplicity, although many metal alkoxides and their derivatives are oligomeric.



III

Although there is no crystallographic proof, the bonding situation is probably similar when α-hydroxy acids are used for the modification of metal alkoxides.

It was recently found that hydroxamate groups provide a particularly inert link between metal alkoxide moieties and organic groups.[8] When $\mathrm{Ti(OPr^i)_4}$ was treated with 1 molar equivalent of benzohydroxamic acid and then with water, the major part of the reaction product contained one hydroxamate ligand per Ti atom. However, a crystalline by-product was obtained (Fig. 1), in which two hydroxamate ligands chelate the (octahedrally co-ordinated) titanium atoms. Co-ordination of metal alkoxides with hydroxamate ligands presently appears to be the hydrolytically most stable way of linking organic groups to metal alkoxide moieties, at least among carboxylate derivatives.

The chemical bond between β-diketonates and metal alkoxide moieties is inherently stronger than that of carboxylates. However, β-diketones with functional substituents are less readily available than functionalized carboxylic acids. Therefore, they will mainly be used for non-functional modification of sol–gel materials. For this purpose they are an excellent choice, however.

Organically modified metal alkoxides with *functional* organic groups were hardly known until recently. As in the case of silicate systems, the introduction of organofunctional groups allows more extensive chemical modifications and the design of materials with totally new properties. The exploitation of non-silicate inorganic–organic hybrid materials has hardly begun, but offers a very rich pool for new materials developments.

Entry into this area is provided by chelating or bridging ligands carrying a functional organic group, as in **I**. The most obvious choice are functionalized carboxylic acids, because they are readily available. Their reaction with metal alkoxides provides carboxylate derivatives $\mathrm{(RO)_yE(O_2C{-}X{-}A)_x}$ where the functional group A is linked *via* the carboxylate group and some spacer X to the metal alkoxide moiety. Among the first well characterized examples were the methacrylate derivatives of $\mathrm{Ti(OR)_4}$ and $\mathrm{Zr(OR)_4}$.[9] The reactive double bonds are fully accessible for later polymerization reactions after sol–gel processing. Some hybrid polymers with titanate or zirconate building blocks were already prepared from these precursors.[9,10]

According to the arguments discussed above, unsaturated precursors with a more strongly chelating link to the metal alkoxide moiety could provide hybrid polymers with even better properties. The first examples were obtained from methacrylamidosalicylicate (α-hydroxycarboxylate link),[11] allylacetoacetate,[5,12] or methacryloxyethylacetoacetate modified metal alkoxides[11] (β-diketonate link). Since hydroxamic acids are easily prepared, also from a variety of functionalized carboxylic acids, their use may turn out to be a stable *and* practical way of linking organofunctional groups to metal alkoxides.

The interest in unsaturated precursors arises from the possibility of preparing inorganic–organic hybrid polymers. However, there are also promising potential applications for materials with other organofunctional groups bonded to metal oxides. Groups capable of binding metal ions or metal complexes can be introduced by the modification of metal alkoxides with α-amino acids having a second functional group. For example, the unco-ordinated amino group of $\mathrm{E(OR)_3(LysO)}$ (E = Ti or Zr, LysO = lysinate) reacts with metal salts to give the complexes $\mathrm{[M\{NH_2(CH_2)_4CH(NH_2)C(O)\overline{OE}(OR)_3\}_n]^{m+}}$ **IV**.[7,13] The titanate- or zirconate-substituted complexes are of the same type and have the same properties as those of corresponding complexes with primary amines as ligands.

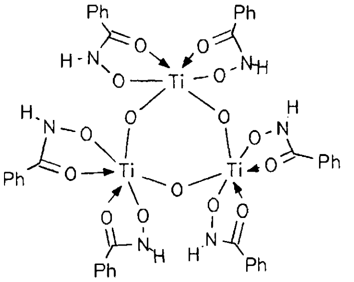
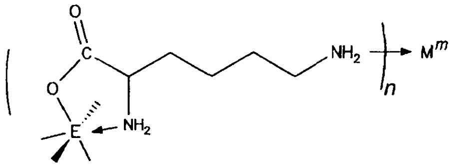


Fig. 1 Schematic structure of $\mathrm{TiO[ONHC(O)Ph]_2}$. The hydrogen atoms were not located; therefore the hydroxamate ligand (H at one of the oxygen atoms) may be bonded in another tautomeric form



IV

Binding catalytically active metal complexes to $\mathrm{TiO_2}$ or $\mathrm{ZrO_2}$ could be attractive not only for heterogenizing these complexes, but possibly also for promoting their activity. Since many catalytically active metal complexes contain phosphine ligands, phosphanyl-substituted metal alkoxides of the type $\mathrm{(RO)_nE{-}X{-}PR_2}$ have been developed for anchoring the metal complexes. Three approaches to prepare such precursors are shown in equations (1) and (2). The preparation of the analogous alkoxysilane $\mathrm{(RO)_3SiCH_2CH_2PPh_2}$[14] is shown in equation (3) for comparison to demonstrate that the strategies are similar.

$$\mathrm{(PrO)_3Zr(O_2CCH{=}CH_2) + PPh_2H \longrightarrow (PrO)_3Zr(O_2CCH_2CH_2PPh_2)} \quad (1a)$$

$$\mathrm{(PrO)_3Zr(O_2CCH_2Cl) + LiPPh_2 \longrightarrow (PrO)_3Zr(O_2CCH_2PPh_2) + Li\,Cl} \quad (1b)$$

$$\mathrm{(RO)_3Zr[O_3SCH_2CMe_2NHC(O)CH{=}CH_2] + PPh_2H \longrightarrow (RO)_3Zr[O_3SCH_2CMe_2NHC(O)CH_2CH_2PPh_2]} \quad (2)$$

$$\mathrm{(RO)_3SiCH{=}CH_2 + PPh_2H \longrightarrow (RO)_3SiCH_2CH_2PPh_2} \quad (3)$$

In the examples, the functional groups are introduced in an indirect way, *i.e.* by modification of a functional group after establishing the E–X link. This is a particularly important option, if, for some reason, organofunctional derivatives of chelating compounds **I** cannot be prepared or if their reaction with metal alkoxides causes problems. For example, addition of $\mathrm{PPh_2H}$ to the acrylic double bond of acrylate-substituted alkoxides or substitution of the chloride in the chloroacetate derivative gave the desired products[15] [equation (2)]. Sulfonic acid derivatives have recently been investigated for linking functional organic groups to metal alkoxides and the first results are very promising.[6,16] The commercially available unsaturated 2-acrylamido-2-methylpropanesulfonic acid readily reacts with $\mathrm{E(OR)_4}$ (E = Ti or Zr);[6] the phosphanyl group can subsequently be introduced by azobis(isobutyronitrile)-initiated addition of the P–H bond of $\mathrm{PPh_2H}$ to the double bond[16] (the reverse order of bond formation, *i.e.* addition of $\mathrm{PPh_2H}$ to the double bond and *then* reaction with the metal alkoxides, is also possible).

The previous discussion shows that the availability of tailored precursors is a key issue for the further development of inorganic–organic hybrid materials with novel properties. Their preparation is a demanding task for inorganic chemistry. The chemical requirements of the precursor molecules are sufficiently defined and the basic chemistry is known. The future task will be to develop a broader molecular basis for such materials.

Design by Variation of the Micro- and Nano-structure

The second aspect of the chemical design of sol–gel materials is the design of their nano- and micro-structure. The primary steps in the sol–gel reaction are very critical in this regard, because in this stage the inorganic building blocks are formed from which the final material is composed. There are several parameters which control sol–gel reactions. The ratio of the hydrolysis and condensation reaction rates and the influence of additives (such as electrolytes, catalysts or chemical modifiers) are particularly important. Not only the type of network (polymer- or cluster-like) can be influenced by adjusting these parameters, but also the density or the degree of cross-linking of the inorganic network. In principle, the elemental chemical steps have to be investigated for each precursor (and for each precursor mixture, because different precursors sometimes mutually influence each other) to get an understanding of the correlation between the properties of the molecular precursors and those of the materials derived from them. However, some general trends are emerging.

A particularly important aspect is the capping of reactive sites to control the size of the primary structures. For example, a cluster-like growth mechanism results in a structure composed of interconnected sol particles (= clusters). Control of the cluster size is therefore very important. This can be achieved by chemical additives blocking reactive sites at the periphery of the clusters and thus inhibiting their further growth. A particularly illustrative example was published by Sanchez and In.[11] Hydrolysis experiments on mixtures of 2-(methacryloyloxy)-ethyl acetoacetate and $Zr(OPr)_4$ with different Zr : β-diketonate ratios showed that this ratio is the key parameter that controls the structure and texture of organic–inorganic hybrid polymers obtained by simultaneous sol–gel processing and radical polymerization of the unsaturated organic groups. A high ratio led to large zirconate building blocks connected by short polymer chains, while a low ratio gave small oxide clusters connected by long polymer chains.

There are several structurally characterized examples of such ‘coated’ clusters.[3] An example from our group is that of $Ti_6O_4(OEt)_8(O_2CCMe{=}CH_2)_8$ formed upon partial hydrolysis of methacrylate-modified $Ti(OEt)_4$[9] (the same structure is also found with other carboxylate groups). It consists of six connected TiO_6 octahedra, sharing edges and corners (Fig. 2). There are five different types of ligands: μ- and μ_3-oxo bridges, terminal and bridging ethoxide ligands and bridging methacrylate ligands. If one takes away all carbon atoms (*i.e.* leaving only the Ti/O skeleton), the structural elements typical of rutile can be recognized. This cluster is ‘coated’ by the organic groups and thus inhibited from further growth (which would not give rutile, but instead amorphous TiO_2; the general reasoning is nevertheless valid). Another important aspect of this structure is that the double bonds of the methacrylate ligands are at the periphery of the hexanuclear cluster and are accessible for polymerization reactions. For example, co-polymerization with methacrylic acid gives organic–inorganic copolymers which contain the titanate clusters.

Aerogels[17,18] are a class of materials the very interesting physical and technical properties of which are nearly exclusively due to their particular microstructure. If $Si(OR)_4$ is treated with water in the presence of a base catalyst the structure grows in a cluster-like manner. An open network with large pores is formed by aggregation of primary and secondary particles. A sketch of the structure is shown in Fig. 3. In the wet gel, as obtained after sol–gel processing, the pores are filled with liquid. Conventional drying of the wet gels results in a large shrinkage, because capillary forces destroy the filigrane structure of the gel. This does not matter for the preparation of dense materials, such as ceramics or glassy materials. However,

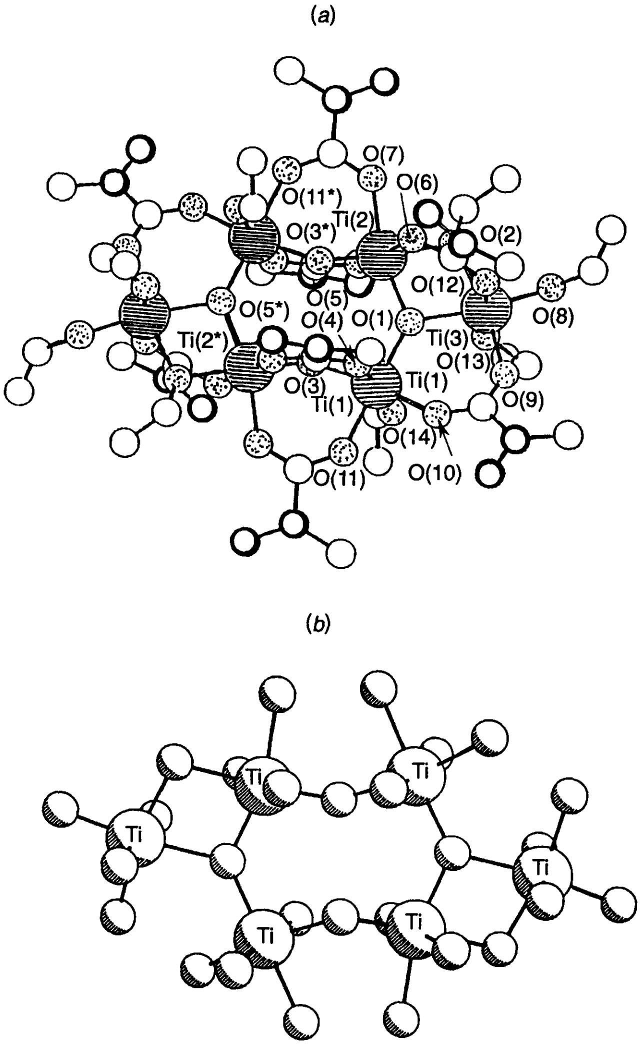


Fig. 2 The structure of $Ti_6O_4(OEt)_8(O_2CCMe{=}CH_2)_8$ (*a*) and the Ti/O core of this cluster (*b*). Reprinted from ref. 9 by permission of the American Chemical Society

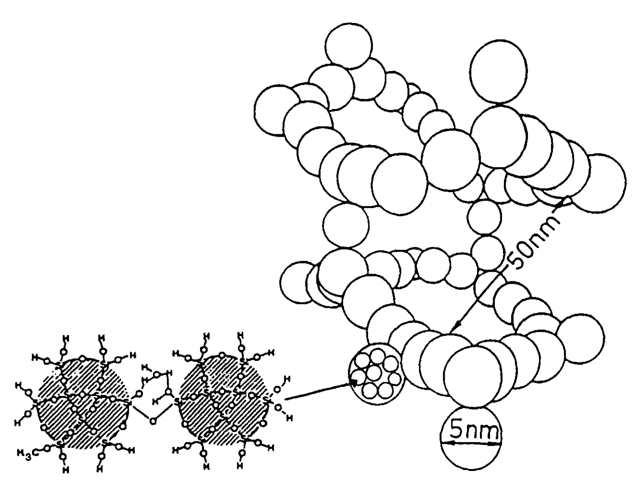


Fig. 3 Structural model of a silica aerogel prepared by base-catalysed hydrolysis and condensation of $Si(OR)_4$[18]

if one wants to keep the highly porous network other drying methods have to be employed. Drying by supercritical fluids is the method most often used. It allows the replacement of the pore liquid by air without shrinking of the gel body. The resulting materials are called aerogels.

The unique properties of silica aerogels are due only to their high porosity, *i.e.* their structure. Technically prepared aerogels have densities around 50–200 kg m^{-3} and porosities around 90%, but densities down to 3 kg m^{-3} have been achieved. Bulk silica aerogels are transparent. The most important physical property derived from the low density is their high heat-insulation capacity which makes them good candidates for novel insulation materials.

Silica aerogels have two disadvantages which somehow inhibit their practical use, their brittleness and their hydrophilicity. The latter is due to the residual Si–OH groups located at the inner surface (Fig. 4, top left). They enable adsorption of moisture and eventually condensation of water into the pores, which, for the reasons mentioned above, physically destroys the gel network. To get moisture-stable aerogels one has to get rid of the surface Si–OH groups. This is done by covering the inner surface with organic groups.

The approach of my group was not to rely on a subsequent hydrophobation (as done by other groups), but to control *both* the structure *and* composition in the sol–gel step.[19] The basic idea was to cap the $SiO_x(OH)_y(OMe)_z$ clusters formed during sol–gel processing of $Si(OMe)_4$ by organic groups and thus to create a hydrophobic inner surface. For this purpose $SiR(OMe)_3$–$Si(OMe)_4$ mixtures (R = alkyl or aryl) were used. The ratio of the two compounds was adjusted so that there are just enough $RSi\equiv$ units to cover the inner surface. Under basic conditions the build-up of the gel network is a two-step process. In the first stage $SiO_x(OH)_y(OMe)_z$ clusters are formed by hydrolysis and condensation of $Si(OMe)_4$, while $SiR(OMe)_3$ basically is a cosolvent. Only when all the $Si(OMe)_4$ is consumed, the organically substituted alkoxide reacts, and the $RSi\equiv$ units condense at the surface of the primary clusters (Fig. 4, top right). Self-condensation of the $RSi\equiv$ units does not play an important role under these conditions and with the appropriate $SiR(OMe)_3 : Si(OMe)_4$ ratio.

The best $SiR(OMe)_3 : Si(OMe)_4$ ratio of course depends on the nature of R and on the density of the aerogels (to some extent also on the supercritical drying conditions). As a rule of thumb, 10–20 mol % $SiR(OMe)_3$ is sufficient to cover the inner surface of the aerogels, but does not affect their nanostructure from which the unique physical properties originate. For $SiMe(OMe)_3$–$Si(OMe)_4$ mixtures it was found that the degree of condensation is not significantly affected when up to 30% of the trialkoxysilane is used in the preparation of the aerogels. One should keep in mind that in an unmodified silica aerogel [made from only $Si(OMe)_4$] the average degree of condensation per silicon atom is only about 3.7, due to residual SiOH and SiOMe groups. Increasing the amount of $SiMe(OMe)_3$ in the starting mixture results in a decrease in the average degree of condensation; monolithic bodies were no longer obtained when the alkoxide mixture contained 80% $SiMe(OMe)_3$.

The organically modified aerogels obtained after supercritical drying are permanently hydrophobic and are therefore not destroyed by moisture. Such aerogels can be kept floating on water for months without any noticeable change. An unmodified silica aerogel would be immediately destroyed on contact with water. A positive side-effect of the organic modification is an improvement in the compliance of the aerogels.

By the organic modification of the aerogels, *i.e.* the proper design of their chemical composition, it is thus possible to add new properties to these materials while retaining their positive properties originating from the open structure. The possibility of varying the chemical composition of aerogels without affecting their special structure opens up totally new perspectives for their applications.

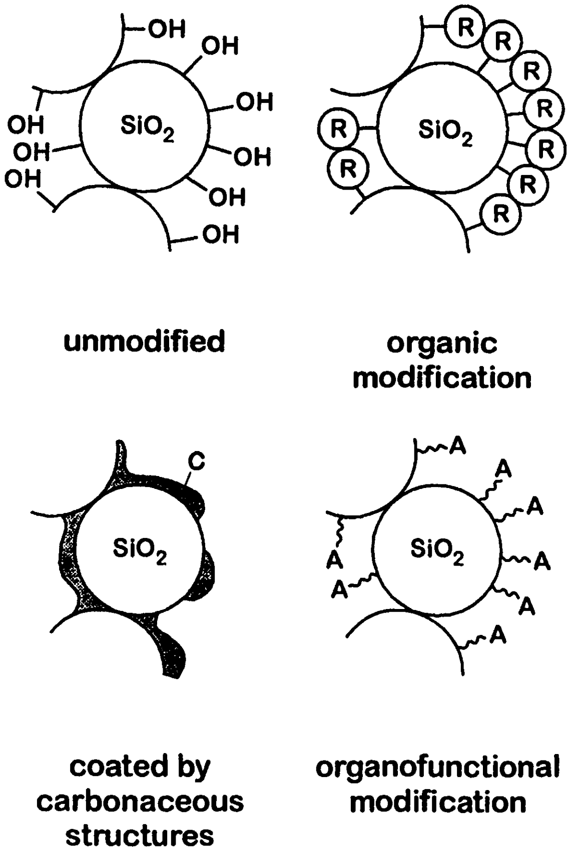


Fig. 4 Chemical modification of the inner surface of silica aerogels. Top left: unmodified. Top right: modification by simple organic groups (alkyl, aryl). Bottom left: generation of nano-sized carbon layers. Bottom right: modification by functional organic groups

Having learnt how to locate organic groups at the inner surface of silica aerogels it was possible to go a step further and introduce *functional* organic groups (A) by using $Si(OMe)_4$–$(MeO)_3Si(CH_2)_nA$ mixtures.[20] This is not a trivial task, because deliberate tailoring of the particular microstructure is much more difficult with organofunctional groups. For electronic or steric reasons, they may influence the build-up of the particular nanostructure during sol–gel processing. Furthermore, the supercritical drying process is hostile to some organofunctional groups. Despite these difficulties functional groups such as A = Cl, CN, PR_2, SH, $OCH_2\overline{CHCH_2O}$, $OC(Me){=}CH_2$, NR_2 or Disperse Red (a non-linear optical dye) were introduced. Such functionalized inorganic–organic hybrid aerogels are expected to lead to novel applications, for example, as catalysts, sensors or ultra-light hybrid polymers. Sol–gel processing of $Si(OMe)_4$–$(MeO)_3Si(CH_2)_nA$ mixtures results in different microstructures of the aerogels depending on the relative reaction rates of $Si(OMe)_4$ and $(MeO)_3Si(CH_2)_nA$. When $(MeO)_3Si(CH_2)_nA$ reacts more slowly than $Si(OMe)_4$ the basic structure of the unmodified aerogels is retained, as discussed above, and the functional groups A are located at the surface of the primary clusters (Fig. 4, bottom right). When it reacts more rapidly (for example, with A = NR_2 or CN) a different microstructure, which still has to be elucidated, is formed. Nevertheless, stable aerogels can be prepared, although some of their physical properties are slightly different.[20]

A final possibility chemically to modify silica aerogels is shown in Fig. 4 (bottom left). The heat transport *via* the solid skeleton and the gas phase in aerogels is low due to their low density and small pore radii. The radiative transport below 20 °C is also low, because silica aerogels absorb heat sufficiently. However, use of silica aerogel for heat insulation at medium temperatures (50–500 °C) requires reduction of the radiative heat transport since the radiation maximum at these temperatures is at 2–8 μm, where silica has a low specific extinction.

Carbon black is very well suited for infrared opacification due to its broad absorption band in the relevant range. Mixing aerogels with carbon black is possible, but the structure and the dimension of the carbon particles play an important role. According to theoretical predictions, the most effective infrared opacification is achieved if the primary aerogel particles are covered by carbon. Nanostructures of this type were created by controlled pyrolysis of organically modified aerogels,[21] which are ideal starting compounds for two reasons. (1) The organic groups are already located at the inner surface. Therefore, there are no diffusion problems. (2) The equal distribution of the organic groups on the inner surface results in a great number of well distributed nucleation centres during pyrolysis and thus leads to small carbon particles.

To achieve a *high carbon content* in the pyrolysed aerogels and to *retain a large percentage of carbon* during pyrolysis, aerogels substituted with large organic groups, preferably aromatic ones, are particularly well suited. The dimensions of the resulting carbon structures are in the lower nanometer range and partially cover the silica nanospheres of the aerogel skeleton (Fig. 4, bottom left). Owing to the arrangement of the carbon structures generated during pyrolysis, a relatively small amount of carbon results in an efficient extinction.

Conclusion

The many possibilities of chemically modifying the precursor systems and the microstructure, and the other inherent advantages of the sol–gel process, allow the deliberate tailoring of materials properties over a wide range. Materials with particularly interesting applications can be prepared starting from organically substituted precursors, particularly those carrying a functional organic group. The manifold options for chemical modification of both the inorganic and the organic groups and for controlling the sol–gel process allow the deliberate preparation of inorganic–organic hybrid materials with special properties. Most of these materials are presently based on alkoxysilanes. Fully to exploit the wealth of this approach for materials syntheses, the underlying chemistry, particularly of non-silicon alkoxides, has to be further developed.

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