Synthesis of Organic−Inorganic Hybrids via the Non-hydrolytic Sol−Gel Process

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In its most common form, the non-hydrolytic sol−gel (NHSG) process involves the reaction of a "metal" halide with an oxygen donor, leading to the formation of an inorganic oxide. The use of NHSG chemistry for the synthesis of organic−inorganic hybrids is in its infancy compared to progress on hybrid synthesis using hydrolytic sol−gel chemistry. To date, most work has been carried out on the synthesis of organically modified inorganic oxides such as ormosils, with very limited effort on oxide−polymer hybrids and no reported activity on incorporation of small organic molecules into oxide networks. In this paper, reports of the use of the NHSG route to synthesize hybrids are reviewed. The key features of the reaction chemistry are noted, along with a discussion of the scope and limitations of NHSG chemistry in comparison with the hydrolytic route. Promising areas for future study are proposed, together with potential applications of these hybrids.

Introduction

While the hydrolytic sol−gel process has been studied extensively over the last 2 decades as a facile route to organic−inorganic hybrids,[1−6] it is only in the last 10 years that the corresponding non-hydrolytic sol−gel (NHSG) process has been recognized as a useful route to inorganic oxides.[7−9] The NHSG route has been evaluated for the synthesis of silica,[10−14] titania,[12−15] and alumina[13−16] and mixed or binary oxides[17−21] such as aluminosilicates and silica−titania systems. Effort on organic−inorganic hybrids synthesized by NHSG chemistry has, however, been limited until very recently. Although the hydrolytic sol−gel route is of considerable utility for the synthesis of hybrids, the development of alternative approaches is important in the context of broadening the scope of hybrid science and accessible products and properties. In this review, recent activity in this area is presented, along with a comparison of the NHSG route with the hydrolytic sol−gel approach.

Non-hydrolytic Sol−Gel Chemistry

The non-hydrolytic sol−gel route involves the reaction of a "metal" halide with an oxygen donor such as an alkoxide, an ether, an alcohol, and so forth under nonaqueous conditions to form an inorganic oxide (Figure 1).[7−9] The byproduct of this reaction is commonly an alkyl halide whose structure depends on the precise nature of the oxygen donor molecule. The electronic factors which control the course of the non-hydrolytic reaction are different from those operating during the hydrolytic sol−gel process. The currently accepted NHSG mechanism proceeds via coordination of the oxygen donor to the central metal atom of the halide, followed by cleavage of the carbon−oxygen bond, instead of metal−oxygen bond cleavage, which occurs during the hydrolytic process.[8−10] One important con-
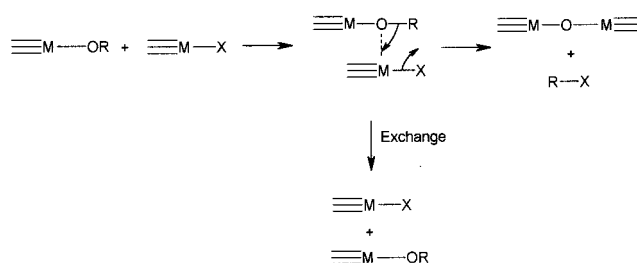

Figure 1. Non-hydrolytic sol−gel route to inorganic oxides.[7−10]

sequence of this is that reactivity differences between different metals, such as silicon and transition metals, may not be the same as those observed in the hydrolytic reaction. The NHSG process may also favor retention of smaller coordination numbers for transition metals and aluminum because of the involvement of nucleophilic substitution reactions. An important side reaction during the NHSG process is the occurrence of ligand exchange reactions (Figure 1),[8−10,22] which can change the kinetics and the mechanistic course of the reaction as well as the precise structure of the product(s).

Several groups[10−21] have reported the synthesis of inorganic oxides via the NHSG route, where M in Figure 1 can be silicon, aluminum, or titanium. The reaction is catalyzed by Lewis acids, with iron(III) chloride being the most commonly used catalyst, although other catalysts may be preferred in specific cases. Because many of the precursor molecules are liquids, the NHSG approach offers the potential to avoid the use of solvents, with their various drawbacks. The reaction also offers the potential for reduction or elimination of residual silanol groups in the product, arising from the different mechanistic course of the reaction compared with the hydrolytic sol−gel route,[8,9,13] but this conclusion is subject to certain provisos (vide infra). The NHSG reactions have normally been undertaken either in sealed tubes under autogenous pressure or under ambi-

ent pressure in flowing nitrogen. It will be shown later that the choice of experimental conditions has important implications for the mechanistic course of the reaction when synthesizing certain types of hybrid.

Non-hydrolytic Sol−Gel Hybrids

In principle, the NHSG route offers access to a range of organic−inorganic nanocomposite products similar to those accessible using the hydrolytic route. In practice, however, differences arising from the nature of the precursors, possible solvent choice, and the different mechanistic courses of the reactions may dictate the type of hybrid which can be made be either route. While the applicability of the hydrolytic sol−gel synthesis has been thoroughly explored over the last 15 years or so,[1−7] the boundaries of the application of the NHSG process to hybrid synthesis have yet to be fully mapped out. The number of literature reports of NHSG hybrid synthesis is tiny in comparison to that of the corresponding hydrolytic approach; however, the limited evidence so far suggests that the NHSG route can provide an attractive alternative to hydrolytic synthesis in some cases and the authors anticipate an upsurge in interest in this approach in the coming years. This activity is most likely in the areas of synthesis of nanocomposite types not yet studied by this approach and in the application of NHSG hybrids with subtly different properties to those accessible via hydrolytic chemistry.

Organically Modified Silicas (Ormosils)

Ormosils are defined as silica or silicate networks which are modified by the covalent attachment of small organic groups to some or all of the silicon atoms in the network. The products where each silicon atom is covalently attached to one organic group are formally the silsesquioxanes of formula $R_2Si_2O_3$. In the ormosils, the organic group is commonly an alkyl chain, an aryl group, or a vinyl group. The synthesis of ormosils has been the subject of considerable research, so far largely confined to the use of the hydrolytic route.[4,23−27] Despite this, the first relevant report of NHSG modification of a silica network by small organic groups dates back to 1956 and the studies of Andrianov et al.,[28] who synthesized a range of alkyl- and aryl-modified silicates and linear polyorganosiloxanes. Various combinations of dimethyldichlorosilane, methylphenyldichlorosilane, phenyltrichlorosilane, phenyltriethoxysilane, and phenylethyldiethoxysilane were reacted in the presence of iron(III) chloride (preferred catalyst) or aluminum(III) chloride catalyst (≤1%) at 95−100 °C in a stepwise heterofunctional condensation reaction. The products were linear, branched, and apparently cross-linked siloxane species. Formation of the products was confirmed by elemental analysis and formation of chloroethane as the byproduct. No evidence was available for the detailed structures of the products obtained.

More recently, Yuh et al.[29] have shown the NHSG method to be useful in the preparation of luminescent gels. Methyl-modified silicates with low hydroxyl contents were synthesized by reacting methyl-substituted silicon halides such as methyltrichlorosilane with *tert*-butyl alcohol. Erbium-doped gels were obtained by dissolving small amounts of anhydrous erbium iodide
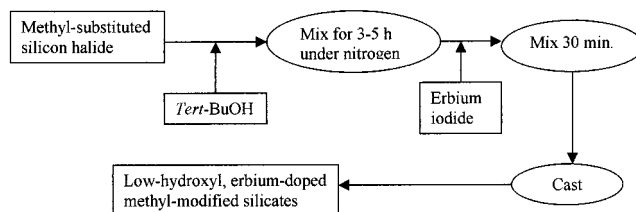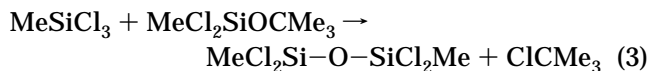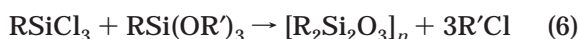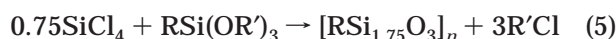

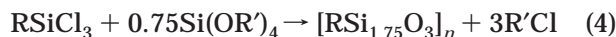**Figure 2.** Preparation of erbium-doped, low hydroxyl content silicate gels.[29]

in the solution prior to gelation (Figure 2). The relevant equations for formation of the ormosil are (1−3)

$$MeSiCl_3 + HOCMe_3 \rightarrow MeCl_2SiOCMe_3 + HCl \quad (1)$$

$$2MeCl_2SiOCMe_3 \rightarrow$$
$$MeCl_2Si-O-SiClMeOCMe_3 + ClCMe_3 \quad (2)$$

$$MeSiCl_3 + MeCl_2SiOCMe_3 \rightarrow$$
$$MeCl_2Si-O-SiCl_2Me + ClCMe_3 \quad (3)$$

The possibility of competitive hydrolytic processes occurring cannot be entirely discounted since the hydrogen chloride produced could catalyze dehydration of the tertiary alcohol, thus forming water. The optimum alcohol:halide ratio for obtaining monolithic gels was 1.5−2.0. The products derived from methyltrichlorosilane were hard and transparent. Using dimethyldichlorosilane as the precursor, there was no gelation, only formation of a diphasic liquid, presumably because of formation of a linear polysiloxane (see later). The erbium-doped gels displayed room-temperature luminescence at 570 nm when pumped at 488 nm, which was explained by the low hydroxyl content of the gels, resulting in reduced quenching. The authors claimed that the different mechanistic course of the NHSG route leads to low hydroxyl-content gels compared to the hydrolytic route; however, the authors note the need to avoid competing reaction with water—this could lead to long-term problems by hydrolysis of any residual Si−Cl bonds. It is also worth noting that Sanchez et al.[30] have shown that the hydrolytic route can be controlled to produce rare-earth-doped, low hydroxyl content silica gels which also show luminescence.

In the late 1990s, groups in Montpellier, France[31,32] and Surrey, England[33,34] independently studied the formation of ormosils using the NHSG route. The two groups used different experimental approaches and, with the exception of the methylsilsesquioxane system, different oxygen donors. Both silicon alkoxides and dialkyl ethers are effective oxygen donors and, where chemically identical products are obtainable using either donor, the choice of donor will depend on factors such as the cost/availability of the donor molecule and the effect of the oxygen donor on the properties of the products. The reactions are normally undertaken at 85−110 °C over a period of minutes to hours in the absence of a solvent and the presence of a Lewis acid catalyst. The metal of the catalyst is incorporated in the ormosil network. The chemistry involved in the synthetic routes is summarized in eqs 4−9. These are class II hybrids according to the classification of Sanchez:[6]

$$RSiCl_3 + 0.75Si(OR')_4 \rightarrow [RSi_{1.75}O_3]_n + 3R'Cl \quad (4)$$

$$0.75SiCl_4 + RSi(OR')_3 \rightarrow [RSi_{1.75}O_3]_n + 3R'Cl \quad (5)$$

$$RSiCl_3 + RSi(OR')_3 \rightarrow [R_2Si_2O_3]_n + 3R'Cl \quad (6)$$

$$2RSiCl_3 + 3R'_2O \rightarrow [R_2Si_2O_3]_n + 6R'Cl \quad (7)$$

$$RSiCl_3 + Si(OR')_4 \rightarrow [RSi_2O_3-OR']_n + 3R'Cl \quad (8)$$

$$SiCl_4 + RSi(OR')_3 \rightarrow [RSi_2O_3-Cl]_n + 3R'Cl \quad (9)$$

The mono- or disubstitution of alkyl groups of varying chain lengths (from methyl to octadecyl), aryl, and vinyl moieties into a silica network has been carried out. Routes (4) and (5) lead to ormosils where every second silicon atom is substituted by an organic group. Routes (6) and (7) produce silsesquioxanes, with every Si atom monosubstituted. Routes (8) and (9) lead to ormosils with residual functionality (chloro or alkoxy) which can in principle be subjected to further chemical conversion. This might be of future value for the synthesis of specifically functionalized ormosils with potential applications in catalysis and sensors.[35]

Although the silsesquioxane products formed by using the different oxygen donors[31,33] can be considered to be chemically identical, the products may have different textural properties, such as porosity. While the effect of various reaction parameters on the textures of ormosils prepared by the hydrolytic route has been the subject of detailed study,[26,36–38] much remains to be learned about the corresponding effects in the NHSG route. Bourget et al.[10] have, however, demonstrated that, for silica xerogels, the same range of textures can be obtained for silica synthesized by both the hydrolytic and the non-hydrolytic route and that the texture of NHSG products depends on the nature of the catalyst and the oxygen donor. Undoubtedly, future work will be directed at demonstrating whether similar effects occur in NHSG ormosil synthesis.

Very different experimental conditions were reported by the two groups. While the Montpellier group used sealed tubes under autogenous pressure,[31] the Surrey group used a flowing nitrogen system at atmospheric pressure.[33] The choice of experimental conditions has a considerable influence on the course of the reaction. The sealed tube route can lead to unwanted byproduct formation, which is insignificant in the case of the other approach—for example, partial Ph_C−Si bond cleavage, leading to the formation of Q species in the phenylsilsesquioxane synthesis, is observed by the Montpellier group,[31] but this cleavage is largely absent in the Surrey synthesis,[33] as shown by ^{29}Si NMR spectroscopy. The reason for these differences probably arises from trapping of the alkyl halide byproduct in the sealed tube, resulting in both Lewis acid catalyzed electrophilic *ipso* cleavage of the phenyl−silicon bond to form cumene and further electrophilic substitution of the cumene by the alkyl halide. In neither approach, however, was there any evidence for either vinyl−silicon bond cleavage or addition reactions across the vinyl double bond during the synthesis of ormosils such as (I). The latter observation provides indirect evidence that the formation of free carbenium ions, proposed as one possible mechanistic course of the NHSG reaction (Figure 3),[13] is unlikely.
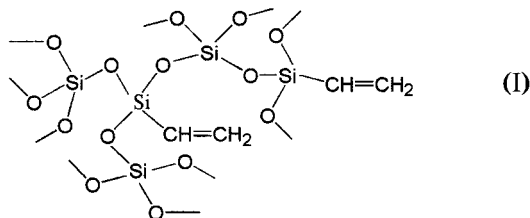

The alkyl carbon−silicon bonds were shown to be totally stable under non-hydrolytic conditions.

Bourget et al.[31] studied the effect of different catalysts on the reaction and showed that the gel time was dependent on the catalyst efficiency, which decreased in the order

$$FeCl_3 > ZrCl_4 > AlCl_3 > TiCl_4 \gg BCl_3$$

The gel time was also found to depend on the type of oxygen donor used, increasing in the order

$$MeSi(OEt)_3 < {}^iPr_2O < Et_2O$$
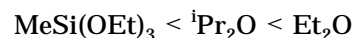
The effect of the ormosil organic group on the gel time appears to be a combination of statistical (reduced functionality on the silicon atom(s)), electronic, and steric factors, with steric effects dominating for bulky alkyl or phenyl groups.[31,33] A further effect of steric interference is observed in the degree of condensation of the resultant ormosils, which is reduced as the organic substituent becomes bulkier.

Although similar hybrids can be made using the hydrolytic method, the non-hydrolytic route has potential advantages for the synthesis of hydrophobic hybrids. For example, in the synthesis of an octyl-substituted silica in a hydrolytic system, the proportion of octyl component which could be incorporated was low; otherwise, phase separation occurred during the reaction.[27] No such problems arose during the non-hydrolytic synthesis of silicas containing bulky groups, even in the case of decylphenylsilsesquioxane[33] and octadecylsilsesquioxane.[31] The only effects of incorporation of such bulky groups are steric effects on the rate of condensation and on the overall extent of condensation. It is interesting to note that the octadecylsilsesquioxane exhibits some ordering by X-ray diffraction and is fusible and soluble.[31] This behavior is attributed to the formation of ormosil particles associated through crystallization of the alkyl side chain.

These ormosils have been shown to be potential precursors to largely microporous silica[33] or to silicon oxycarbide[31] via pyrolysis at elevated temperatures. Silica of >80% microporosity and surface area close to 500 m^2 g^{-1} can be obtained in this way. Silicon oxycarbide formation arises from Si−O/Si−O and Si−C/Si−O exchange reactions, leading to loss of volatile silicon species, the extent of which is dependent on the nature of the catalyst and the oxygen donor.

Synthesis of organically modified aluminosilicates ("ORMALSILs") using non-hydrolytic sol−gel chemistry has also been reported.[39] In this case, an alkyltrichlorosilane was reacted with aluminum(III) isopropoxide in a solvent-free synthesis using iron(III) chloride as the catalyst (eq 10). The ormalsil reactions showed similar gel time effects to those found in ormosil synthesis.
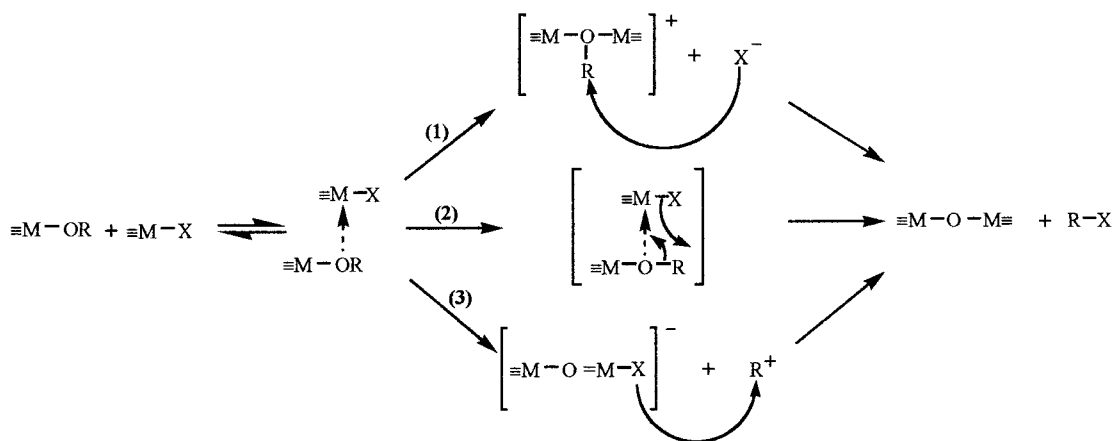
Figure 3. Proposed mechanistic course of the non-hydrolytic sol−gel route.[13]

$$RSiCl_3 + Al(OR')_3 \rightarrow [RSiAlO_3]_n + 3R'Cl \quad (10)$$

Although it has not been proven, the non-hydrolytic route has the potential to produce hybrid aluminosilicates which are more homogeneous on a molecular level[17] than those accessible by the hydrolytic approach, where the different hydrolysis rates of the precursors can result in inhomogeneities.[40]

Silica−Polymer Hybrids

While the hydrolytic sol−gel synthesis of hybrids of silica with a wide range of different polymer types has been the subject of extensive study,[1−3,5,6] the use of the non-hydrolytic route for the synthesis of analogous hybrids is an area of largely untapped potential. The different kinetic and electronic factors operating during the reactions and differences in compatibility between the polymer and the sol−gel precursors and intermediates all suggest that, for a given polymer system, the nature of the hybrid obtained by NHSG chemistry may be quite different from that obtained by the hydrolytic route. For that reason alone, a detailed study of the applicability of the NHSG process to the synthesis of polymer−silica hybrids seems justified. The NHSG route should offer a complementary approach to the hydrolytic process, which may allow the synthesis of hybrids not easily obtainable by a hydrolytic method, where use of water can cause compatibility problems.[9] One potential problem which would need to be considered is that of oxygen-containing polymers becoming involved in the chemistry as oxygen donors.

Preliminary studies[39] have shown that it is possible to polymerize styrene and the silica precursors (tetraethoxysilane and silicon(IV) chloride) simultaneously using iron(III) chloride as the catalyst for the non-hydrolytic sol−gel reaction and AIBN as the radical initiator for styrene polymerization (Figure 4). Hybrids were prepared from precursor mixtures containing up to 50 wt % styrene. ^{29}Si NMR spectroscopy confirmed the presence of mainly Q^3 and Q^4 silica species, while polystyrene formation was confirmed by ^{13}C NMR spectroscopy. Thermogravimetric analysis suggested that the 30% polystyrene hybrid was stable up to $\approx$400 °C. The precise microstructure of the products was not determined and no further properties of the hybrids were reported.
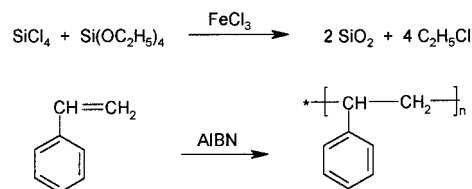

Figure 4. Non-hydrolytic synthesis of polystyrene−silica hybrids.[39]

Using hydrolytic sol−gel chemistry, it is possible to synthesize the silica−poly(dimethylsiloxane) (PDMS) system,[41,42] which can be varied from a hard, glassy solid to a rubbery product depending on the ratio of PDMS to silica.[43,44] Using non-hydrolytic sol−gel chemistry, it has been shown that it is possible to synthesize the silica and the dimethylsiloxane segments in situ using iron(III) chloride as the catalyst for both the cationic ring-opening polymerization of the cyclic siloxane, D_3, and the sol−gel reaction.[39] Solid hybrids were obtained using an initial mass % of D_3 ranging from 1 to 50%, based on the total mass of reactants. The "idealised" reaction is shown in Figure 5. These products showed no evidence of elastomeric behavior, even at 50% siloxane content. The chemical structure of the products was confirmed by infrared and solid-state NMR spectroscopies. Together with the physical properties of the hybrids, the results suggested formation of *oligomeric* dimethylsiloxane−silica hybrids.

As part of their studies on poly(ferrocenylsilane)s with specific electrochemical properties, Corriu and co-workers[45] have synthesized 1,1′-ferrocenediyldialkoxysilanes and their corresponding polymers. The ferrocenyl compounds could be incorporated into a silica matrix by a non-hydrolytic sol−gel reaction (Figure 6). Cyclic voltammetry showed that the hybrids had electrochemical behavior expected of ferrocenyl species, but with a shift in potential.

A number of studies have been concerned with the use of the NHSG route to synthesize siloxane polymers, and because of the relevance of this work to the previous section and the fact that these polymers can be regarded as methyl-modified silicates, a discussion of this work is included here. The early work of Andrianov et al.[28] has already been mentioned. Eleven years later, the importance of equilibrium exchange reactions (see Figure 1) scrambling the ligands prior to condensation of methyltribromosilane with methyltrimethoxysilane
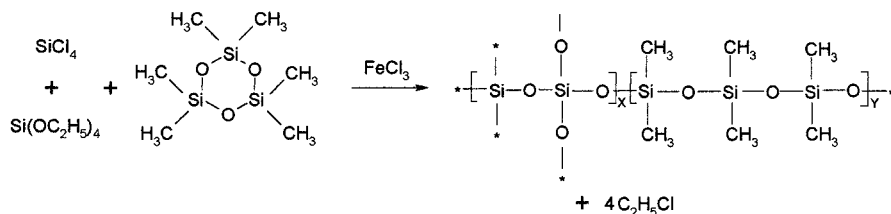
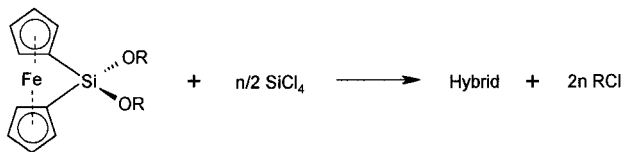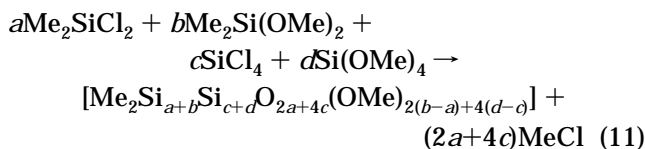**Figure 5.** Synthesis of silica−*oligo*dimethylsiloxane hybrid.[39]

Figure 6. Synthesis of a ferrocenyl−silica hybrid.[45]

to form Si−O−Si linkages was discussed.[46] The reaction led to the formation of a colorless, fluid methoxypolymethylsiloxane. Corriu et al.[47] in 1994 confirmed the importance of the exchange reactions in the synthesis of copolysiloxanes by the polycondensation reaction exemplified in Figure 7. Use of a reactive alkoxy derivative (R = Ph_2CH-) in a solvent-free process resulted in relatively facile formation of the quasi-random siloxane copolymer. The reaction can be catalyzed by species such as fluoride ion, which catalyzes nucleophilic attack at the silicon atom by formation of complex anions with an increased positive charge on the central silicon atom. The reaction is marked by an absence of degradative side reactions which might limit the chain growth. The same group has used analogous chemistry to synthesize alkoxy-functionalized, liquid polysiloxane D/Q resins catalyzed by Lewis acids.[48] The chemistry involved is represented in eq 11. Use of a

$$a\text{Me}_2\text{SiCl}_2 + b\text{Me}_2\text{Si(OMe)}_2 + \\ c\text{SiCl}_4 + d\text{Si(OMe)}_4 \rightarrow \\ [\text{Me}_2\text{Si}_{a+b}\text{Si}_{c+d}\text{O}_{2a+4c}(\text{OMe})_{2(b-a)+4(d-c)}] + \\ (2a+4c)\text{MeCl} \quad (11)$$

catalyst such as iron(III) chloride or aluminum(III) chloride led to considerable formation of dimethyl ether as a result of secondary condensation reactions (eq 12) catalyzed by the Lewis acid. Assessment of a large

$$\equiv\text{Si}-\text{OMe} + \text{MeO}-\text{Si}\equiv \rightarrow \equiv\text{Si}-\text{O}-\text{Si}\equiv + \text{Me}_2\text{O} \quad (12)$$
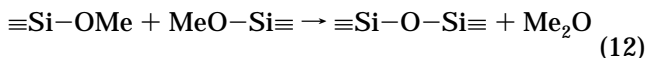
number of potential catalysts led to the choice of zirconium(IV) chloride as offering the best compromise between selectivity and reaction rate. Again, major redistribution reactions of all the Si−X bonds, other than stable Si−Me bonds, occurs, leading to polymers where the Si−OMe and Si−O−Si bonds are randomly distributed around D and Q units. Another route to siloxane copolymers has been described by Japanese workers,[49] although in this case the hybrid-forming step occurs as a postpolymerization reaction. In this process, a polymetallosiloxane such as polyzirconosiloxane (PZS) is formed by reaction of silicic acid with the metal(IV) chloride. The PZS is then esterified with an alcohol, followed by non-hydrolytic condensation (silylation) with dimethylphenylchlorosilane to give the organically modified product (Figure 8), which was synthesized to aid
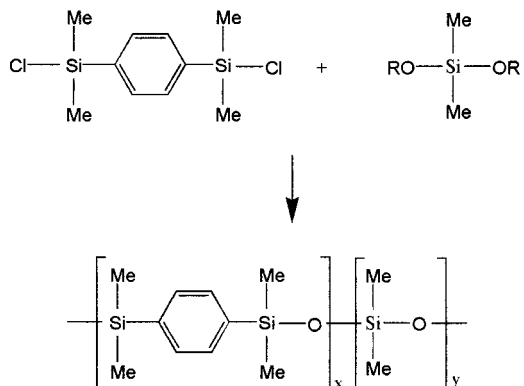

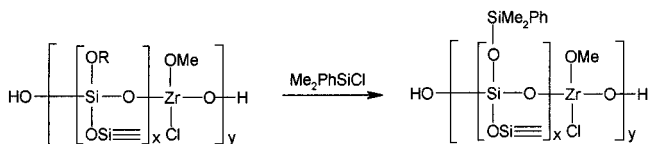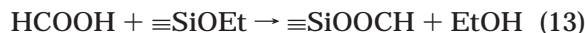**Figure 7.** Copolysiloxane synthesis using the non-hydrolytic sol−gel method.[47]

Figure 8. Synthesis of silylated polyzirconosiloxane.[49]

analysis of the precursor. This product is also a possible precursor to other hybrid materials.

It is apparent that the non-hydrolytic route does have the potential to produce silica−polymer hybrids in the case of siloxanes, polystyrene, and ferrocenyl polymers and further investigation of these reactions and the nature of the products is warranted. It is necessary to probe the scope of the NHSG process for the synthesis of such hybrids, including a study of systems such as acrylic hybrids, where both the acrylic monomer and polymer are capable in principle of acting as oxygen donors to the silicon halide. The effect of introducing covalent bonding between the organic and inorganic phases, for example, in the polystyrene case above, should also be studied, as has been done extensively for hydrolytic hybrids. The possible effects of ligand exchange reactions on the structure of the products needs to be considered.

A somewhat different approach to synthesizing hybrids in a nonaqueous system has been described by Sharp of Du Pont.[9,50−52] It is arguable whether this is truly a "non-hydrolytic" approach since water is generated in situ during the reaction; however, it is included here for the sake of completeness since the initial reaction conditions are nonaqueous. This route involves the use of a strong carboxylic acid such as formic acid as solvent and catalyst for the sol−gel process, the acid also acting as a good solvent for a number of polymer systems. Some of the main reactions involved in this chemistry are shown below (eqs 13−16),[50,51] water being formed in the esterification reaction shown in eq 14.

$$HCOOH + \equiv SiOEt \rightarrow \equiv SiOOCH + EtOH \quad (13)$$

$$EtOH + HCOOH \rightarrow EtOOCH + H_2O \quad (14)$$

$$\equiv SiOEt + H_2O \rightarrow \equiv SiOH + EtOH \quad (15)$$

$$\equiv SiOH + \equiv SiOOCH \rightarrow \equiv SiOSi \equiv + HCOOH \quad (16)$$

The condensation reaction represented in eq 16 is fast in comparison to the other condensation reactions which can occur during the sol–gel process. Formic acid readily dissolves several types of polymer (e.g., poly-(vinyl alcohol), poly(methyl methacrylate), cellulose acetate, and poly(vinyl pyrrolidone)) and the route permits access to a range of silica–polymer hybrids, the rapid network formation apparently inhibiting phase separation.[51] A side reaction can result from esterification of hydroxyl groups in the polymer by the formic acid. The hybrids have thermal and mechanical properties which can differ significantly from those of the parent polymer. Incorporation of the silica network increases the glass transition temperature and room-temperature modulus and can also lead to increases in toughness. Hybrid coatings exhibited good abrasion resistance and hybrid films had much reduced oxygen permeability relative to neat polymer.

Use of this chemistry allows hybrid synthesis to be extended to the use of fluorinated materials which would be difficult or impossible to synthesize in an aqueous system.[52] For example, an amorphous fluoropolymer (Teflon AF) can be incorporated into a silica hybrid prepared by reaction of a polyfluoroalkoxysilane with trifluoroacetic acid in a perfluorinated solvent. Similarly, fluorinated ormosils can be generated in situ in swollen rubbers from infused fluoroalkyl-functionalized silanes and formic acid.

Sharp has also used the formic acid approach to synthesize so-called star gels, which are hybrids which behave like a cross between glasses and cross-linked rubbers.[52] A typical precursor is shown below (II). The

(II)
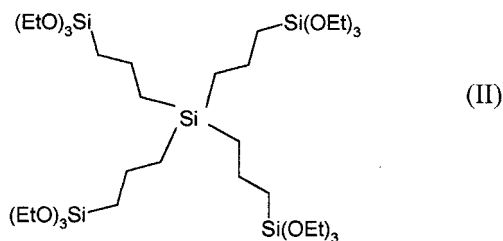
resultant glasses are transparent and tough. The reaction of transition metal alkoxides with carboxylic acids also provides a possible route to hybrids, as discussed under "Other Inorganic Oxide Hybrids".

Silica–Small Molecule Hybrids

Incorporation of small organic molecules into sol–gel silica networks by physical entrapment or grafting allows the properties of the silica to be modified in a specific way, for example, by changing the optical or electronic properties of the silica glass.[53,54] Such an approach is attractive for the development of new sensor technologies[54,55] and is an active research area in the field of hydrolytic hybrids. The authors are not aware of any such activity in NHSG research. One possible
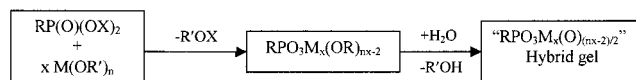

**Figure 9.** Synthesis of metal oxide–phosphonate hybrids.[56]

limitation, of course, is the problem of involvement of oxygen-containing organic molecules in the NHSG process, with the result that the desired property enhancement is not attained. This limitation aside, it should be recognized, however, that the NHSG reaction could have considerable merit in the synthesis of hybrids where the organic species is highly sensitive to the presence of water. We await developments in this field.

Other Inorganic Oxide Hybrids

The non-hydrolytic sol–gel process has recently been extended to the synthesis of novel metal oxide–phosphonate hybrids.[56] The synthesis is a two-step process involving initial non-hydrolytic reaction of a metal alkoxide with a phosphonic acid or ester to form the M–O–P bonds (eq 17), followed by conventional hydrolytic reaction of the residual alkoxide groups to form the M–O–M linkages (Figure 9). In the case of titania–

$$M-OR + XO-P \rightarrow M-O-P + ROX$$
$$[X = H \text{ or } SiMe_3] \quad (17)$$
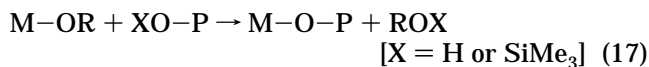
phenylphosphonate hybrids prepared from reaction of titanium(IV) isopropoxide with either phenylphosphonic acid or phenylbis(trimethylsilyl)phosphonate, the results demonstrate complete non-hydrolytic condensation to Ti–O–P bonds. The isolated cluster compound III

(III)
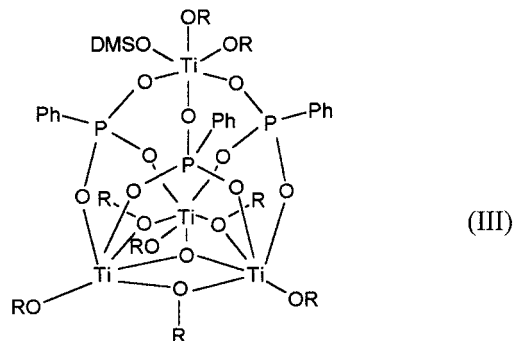
appears to be an important intermediate in the reaction. Analysis of the final hybrid gels shows that the Ph–P bonds are unaffected by the reaction and that the products are not layered compounds, but probably homogeneous dispersions of phenylphosphonate groups within the titania network. The hybrids are chemically inert to a range of pH's from 1 to 10.

Layered metal oxide–phosphonate hybrids can also be made by a related route.[57] Titanium, zirconium, and tin phosphonates have all been synthesized by non-hydrolytic reaction of the metal(IV) halide with a dialkyl- or dichlorophenylphosphonate or methylphosphonate (e.g., eq 18). When X = H, an excess of the

$$TiCl_4 + 2RP(O)Cl_2 + 4R'OX \rightarrow$$
$$Ti(O_3PR)_2 + 4R'Cl + 4XCl \quad [X = R' \text{ or } H] \quad (18)$$
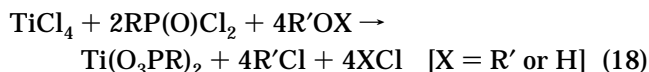
alcohol increased the degree of condensation of the product. X-ray diffraction showed that the compounds

Table 1. Comparison of the Hydrolytic and Non-hydrolytic Sol−Gel Routes

hydrolytic	non-hydrolytic
facile, low-temperature process	facile, low-temperature process
homogenizing solvent used	potentially solvent-free
use of water	reactive reagents
water, alcohol formed	alkyl halide formed
good for ionic and O-containing species	potential problem of O-containing species
limited compatibility of hydrophobic species	no problem with hydrophobic ormosils
well-established	new technology
	good for water-sensitive species

are layered, but poorly crystalline. A side reaction observed in the case of the zirconium and tin phenylphosphonates is the formation of alkylphenyl groups by Friedel−Crafts alkylation of the benzene rings by the alkyl halide byproduct, catalyzed by the zirconium(IV) and tin(IV) chlorides. This observation confirms the importance of careful catalyst selection in specific cases, particularly when it is noted that in the synthesis of polysiloxane D/Q resins (vide supra), zirconium(IV) chloride was found to be the most selective catalyst in minimizing a (different) side reaction. It is clear that catalyst choice is system specific and needs careful consideration when embarking on NHSG synthesis of new materials. The chemistry described here was also applied to the synthesis of silicon phosphonates, although definitive evidence for the formation of layered structures was not found. Because of the hydrolytic instability of Si−O−P bonds, the NHSG chemistry offers a potential solution to the problem of synthesizing silicon phosphonates by a sol−gel route.

The non-hydrolytic reaction of alkoxides with carboxylates is known to lead to the formation of metal−oxygen−metal linkages (eq 19).[58] Recently, the study

$$MOR + MO_2CR' \rightarrow M-O-M + R'CO_2R \quad (19)$$
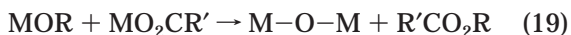
of transition metal oxo clusters containing carboxylate groups has attracted interest because of their potential as well-defined building blocks for subsequent transformation to oxides and organic−inorganic hybrids. The metal oxo compounds are made by non-hydrolytic condensation of the metal alkoxide with the carboxylic acid. A range of titanium oxo species has been reported[59−62] and similar oxozirconium species have also been synthesized.[63] The clusters are effectively nanotitania or zirconia surrounded by carboxylate ligands. Where the clusters contain ligands such as acrylates, conversion to polymeric hybrids can be envisaged. Ketones have also been shown to act as oxolation sources in the non-hydrolytic conversion of titanium and zinc alkoxides to titanium oxo-alkoxo complexes[64] and to zinc oxide,[65] respectively.

Comparison of the Hydrolytic and Non-hydrolytic Sol−Gel Routes

A summary of some of the features of the hydrolytic and non-hydrolytic sol−gel processes for the synthesis of hybrids is presented in Table 1. Some other features of the NHSG route have already been discussed, for example, the importance of catalyst selection to reduce byproduct formation and optimize formation of the desired product. The latter is also typical of the hydrolytic process, albeit with very different types of catalyst. To decide which of the two routes to use for a particular hybrid synthesis, it is necessary to consider the nature of the hybrid to be synthesized and relevant factors such as water sensitivity of any of the components, compatibility issues, and so forth. The choice of route may be obvious in some cases, while in others, subtle differences between the products obtainable by each route may dictate the method selected. A combination of the two routes, used sequentially, might also be beneficial in terms of control of the structure of the final product.

The Future

The full potential of the non-hydrolytic route for the synthesis of organic−inorganic hybrids has yet to be evaluated. The main areas where future research activity is anticipated are as follows:

(1) Further detailed study of the synthetic scope of the ormosil synthesis and the properties of the products.

(2) A thorough investigation of the boundaries of the application of the NHSG route to the synthesis of inorganic oxide−polymer hybrids.

(3) Extension to the incorporation of small organic molecules into oxide matrixes, particularly in the case where exposure of the "encapsulant" to hydrolytic conditions would be problematic.

(4) Further extension to binary or mixed oxide hybrids.

(5) Combination of the NHSG and hydrolytic processes to produce products such as coatings from controlled structure intermediates (sols).

While it is highly unlikely that the non-hydrolytic route will replace the conventional route in most cases, it is likely that it will offer a complementary approach, which may allow the synthesis of hybrids not easily obtainable by a hydrolytic method. In this respect, the development of the non-hydrolytic sol−gel route has added another "string to the bow" of the sol−gel hybrid chemist.

In contrast to the situation with hydrolytic sol−gel hybrids, where potential applications are under serious consideration (and, indeed, commercialization of coating systems is already underway), no application work on non-hydrolytic hybrids has been described to date. It is obvious that many non-hydrolytic hybrids may find application in identical areas to those proposed for their hydrolytic analogues. An example is in coatings, where rheology modification is feasible by use of solvents and partially precondensed intermediates, such as chloroalkoxides. In structural applications, hybrids could be processed by moulding of preformed products (such as the polystyrene−silica hybrid described above) or by in situ polymerization [using a polymerizable R group]. Interest in the optoelectronic performance of NHSG hybrids has already been noted.[29] The hybrids are also potential precursors to nanoporous inorganic oxides, with possible applications in catalysis and separations.

While much work remains to be done in understanding the scope and limitations of the NHSG route to organic−inorganic hybrids, the authors believe that there is sufficient evidence of its unique synthetic capabilities to provide confidence that this approach will attract increased attention in the future. Further exciting discoveries remain to be made.

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