CHEMISTRY OF MATERIAL PREPARATION BY THE SOL–GEL PROCESS

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A survey over the role of chemistry in sol–gel processing is given. The basic chemistry of the sol–gel process is complex due to the different reactivities of the network forming and the network modifying components and the wide variety of reaction parameters. Despite the important progress in the investigations of the mechanisms of hydrolysis and condensation, a direct relation of reaction parameters to material properties is still very difficult.

1. Introduction

The sol–gel process has become a widely spread research field during the last two decades. Since the early work of Geffcken [1], Roy [2] and Dislich [3] the fields of investigation have widened dramatically. Thus, it is almost impossible to review the important literature in a comprehensive article. A good survey over the state-of-the-art can be provided by the conference proceedings: International Workshop on Glasses and Glass-Ceramics from Gels [4–6], Material Research Society Symposium Proceedings [7,8] and Conference on Ultraprocessing of Glasses, Ceramics and Polymers [9–11] and literature cited therein. History tells us that two research fields, namely chemistry and material science have to be combined in order to make good progress in the field.

Basically the sol–gel process means the synthesis of an inorganic network by a chemical reaction in solution at low temperature. Inorganic networks can also be built up by other chemical reactions, e.g. from the vapor phase or by high temperature processes like melting. The sol–gel process means, too, the formation of an (at least in the first step) *amorphous* network, in opposition to crystallization processes from solution. Sometimes, it is not very simple to distinguish between crystallization and amorphous network formation: in the case of alumina, crystalline phases appear at low temperatures, e.g. $< 100°C$

in solution, despite the fact that the basic network forming step may be an *amorphous* one.

Precipitation of hydroxides, mostly amorphous, is a long and well-known technique in chemistry, especially to separate different elements from multicomponent solutions. Based on their different basicity, hydroxides can be precipitated at different pH values. Thus, most of the transition metals and the group III and VI elements can be precipitated as gel-like hydroxides in aqueous solutions, but that chemistry has not become known as sol–gel chemistry. This is due to the fact that the significance for the synthesis of non-metallic inorganic materials was first pointed out by material scientists and most of these hydroxide precipitation methods are aimed at analytical procedures.

The most obvious features of this reaction, the transition from a liquid (solution or colloidal solution) into a solid (di- or multiphasic gel) led to the expression "sol–gel process". This type of reaction of course is not necessarily restricted to an aqueous system, but aqueous reactions like these have been known for a very long time.

Natural processes like the formation of minerals such as agate and chalcedon [12,13] have been performed by dissolution and precipitation of gel and formation from colloidal siliceous acid solutions. The formation of aluminum hydroxides from aluminum acetates is still used nowadays for medical purposes. These are only a few examples for the formation of inorganic polymers by a

sol–gel procedure. Any precursor, which is able to form reactive "inorganic" monomers or oligomers can be used for sol–gel techniques. Even finely divided silica particles can be peptisized and used for the preparation of sols. Therefore, it is necessary to generate appropriate surface charges in order to prevent coagulation and precipitation.

Most work in the sol–gel field has been performed by the use of alkoxides as precursors. Alkoxides provide a convenient source for "inorganic" monomers which in most cases are soluble in common solvents.

Another advantage of the alkoxide route is the possibility to control rates by controlling hydrolysis (1) and condensation by chemical means and not by surface or colloid chemistry. Eq. (2) shows the most important condensation reactions: The condensation of two M–OH groups or the reaction of an M–X with an M–OH group.

$$\equiv M-X + H_2O \rightarrow \equiv M-OH + HX, \qquad (1)$$

M = metal or Si; X = reactive ligand like halogen, OR, NR_2, acylate;

$$\equiv M-OH + X-M\equiv \rightarrow \equiv M-O-M\equiv + HX,$$

$$\equiv M-OH + HO-M\equiv \rightarrow \equiv M-O-M\equiv + H_2O. \qquad (2)$$
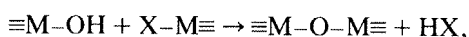
The chemistry of processes like this should be more easily controlled than colloid chemistry phenomena like surface charges or species adsorbed on surfaces of particles. That means, that at least within the first step of the reactions, the alkoxide route or even better, the route of using latent reactive monomers could be advantageous compared to the route using colloids as starting materials. Another advantage of the latent monomer route is the solubility of these monomers (e.g. alkoxides, halogenides, acylates) in a variety of organic solvents expecially alcohols. Alcohols enable a convenient addition of water to start the reaction according to eq. (1).

To summarize, one can say that the present state-of-the-art in the sol–gel field can clearly describe the basic features of the sol–gel process. Since a strong input comes from application related material science, these features are related to application, too. It is a surprising fact, that basic

chemistry became more and more involved in sol–gel related questions only recently after a tremendous amount of sol–gel work was done by material scientists.

The efforts of material scientists result from the potential advantages of the sol–gel process for material synthesis which can be summarized as follows:

- it provides an easy way to purify precursors,
- it provides an easy way to get homogeneous distributions of precursors,
- it provides an easy way to introduce trace elements,
- it allows the use of chemistry to control reactions,
- it allows the formation of a "pre"-inorganic network in solution,
- it allows the introduction of permanent organic groupings in solution (thus leading to inorganic–organic hybride materials),
- it allows the densification to inorganic solids at comparitively low temperatures (due to the "pre"-networks),
- it allows the adjustment of appropriate viscosities for coatings,
- it allows the preparation of new glass compositions (due to low temperature processing thus avoiding high crystallization rate ranges),
- it allows the synthesis of active ceramic powders.

These potentials led to numerous endeavours to enhance applications. A comprehensive survey is given in [14]. Of course, there are a lot of restrictions with respect to applications: cost of precursors, difficulties in the synthesis of monoliths, and last but not least, the difficulties in chemistry with respect to tailoring properties, to reproducibility or to processing. Thus, much effort is devoted to investigations of the reaction mechanisms of hydrolysis and condensation, and as a result of this, numerous new and interesting results were obtained, partially due to better analytical equipment (e.g. FT-IR, NMR, GC, MS, Raman, SAXS, SEM, STEM). But despite this effort, even the simple looking reaction of hydrolysis and condensation of $Si(OR)_4$ cannot be closely followed on a molecular level beginning from the monomer or oligomer to the polymer. This indicates the wide range of chemistry involved in sol–gel

material processing, especially if the different sol–gel steps are taken into consideration:

sol – gel processing steps	*chemistry involved*		
precursors	organometallic chemistry, coordination chemistry, inorganic chemistry, organic chemistry,	}	latent monomers
	colloid chemistry, inorganic chemistry,	}	colloids
hydrolysis	organometallic chemistry, inorganic chemistry, physical chemistry,		
condensation	inorganic chemistry, colloid chemistry, polymer chemistry,		
gelation	colloid chemistry, inorganic chemistry, physical chemistry,		
drying densifying heating incorporation of organics	inorganic chemistry, organic chemistry, chemical engineering, organic chemistry.		

The number of possible precursors, the number of composition possibilities, and the number of reaction parameters within the different steps lead to an immense number of variables. That means that the chemistry behind this is a very complex one. In addition to this, characterization of reaction mechanisms, intermediates and even polymers becomes difficult, too. A system, once started e.g. by hydrolysis cannot be stopped again, even if the addition of water is stopped. Rearrangement of the oligomers or polymers can take place over a long period. In a later state unsoluble, three-dimensional cross-linked structures or particles appear, which cannot be analysed by the common means of polymer analysis. Summarizing this, the overall chemistry still appears as a black box. We know what we put into this box and we can analyse the result, but the steps in between are weakly illuminated.

One can conclude from this that for material synthesis in most cases only a limited number of variation parameters can be investigated and it is necessary to find out the *important* parameters

with respect to the desired *material properties* in a screening process. In order to attain these objectives experience with sol–gel chemistry (so-called chemical feeling) is still indispensable. But this field of material development must not be restricted to chemistry. The research is interdisciplinary. It involves, in many cases, besides chemistry: chemical engineering, material science, mineralogy, physics or even engineering and computer science.

In the following, the attempt is made not only to illustrate some special chemical aspects of sol–gel synthesis from the material science point of view and to point out how chemistry can be used but also the problems which arise and which have become clear due to the immense work of numerous scientists.
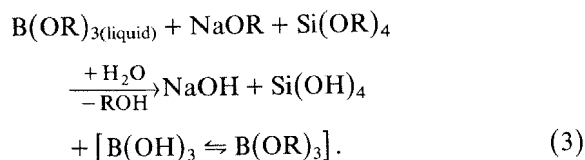
2. General considerations

2.1. Parameters

The complexity, as indicated above, is mainly caused by the numerous parameters involed in a sol–gel material synthesis. One can distinguish between three important groups of parameters influencing the material properties:
- composition,
- reaction (from start up to gel formation),
- processing (after gel formation).

2.1.1. Composition

The composition can be defined by the starting compounds. But this apparently simple fact involves different complications in practice, especially if alkoxides with low boiling points are used as precursors: volatile compounds can be evaporated during the sol–gel reaction, e.g. boron during the synthesis of borosilicate glasses:

$$B(OR)_{3(liquid)} + NaOR + Si(OR)_4$$

$$\xrightarrow[-ROH]{+H_2O} NaOH + Si(OH)_4$$

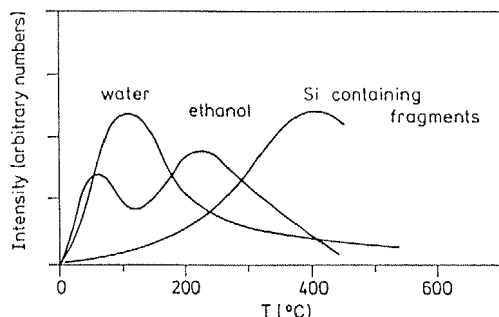$$+ [B(OH)_3 \leftrightharpoons B(OR)_3]. \tag{3}$$

Since there exists an equilibrium reaction which

Fig. 1. Volatiles detected in a $(CH_3)SiO_3/SiO_2$ cocondensate by MS analysis.

easily follows its thermodynamics, a loss of boron, especially in open systems, can be observed and has to be taken into account.

Another possibility for the loss of starting material is the incomplete reaction of a slowly reacting compound such as $Si(OR)_4$, especially in a neutral media or with higher alkyls such as R: unreacted or not completely reacted monomers remain and evaporate during drying and heating. The same results can be observed if the incomplete reaction takes place from equilibrium for the same reasons as indicated in (3), for example, due to the choice of disadvantageous parameters (e.g. low water content, high dilution with alcohols as solvents): this can lead to a high content of oligomers (soluble or volatile) and a decrease in the yield, in the case of $Si(OR)_4$ as precursors to the yield of SiO_2. Reesterification can also lead to the formation of volatiles. Oligomer analysis of cocondensates as described in [15] indicates (fig. 1) that the formation of oligomeric silanes at least might be partially due to the formation of alcohol by further condensation at 150–200 °C. Detailed analysis of the volatile Si-containing fragments led to the conclusion that partially hydrolysed monomers as well as different types of oligomers were present. Side reactions like this can affect compositions as well as homogeneity. Proper choice of reaction conditions and precursors can help to overcome these problems. Summarizing, one can say that the genuine composition can change by volatile or partly volatile species or intermediates being evaporated during processing, by soluble species (e.g. during washing procedures) or by back reaction.

2.1.2. Gel formation

It is something like a rule in sol–gel processing to try to obtain the most homogeneous distribution of components during the gelation step, independent of the shape of the material to be produced (e.g. small particles like ceramic powders, films or monoliths). Desired "inhomogeneity" like phase separation or crystalline phases in general can be very easily introduced by thermal treatment. Thus, one tries to obtain amorphous gels. It is an interesting question, whether a given system is able to form homogeneous gels or not. The ability of systems to form glass has been well investigated and a couple of theories have been developed (e.g. by Zachariasen or Dietzel). Once the systems are above the liquidus temperature, one can predict quite precisely whether the system forms stable glasses or not. Rapid quenching has enlarged the range of glass forming systems. Unfortunately, despite some analogies, these ideas cannot be transmitted to their gel forming ability without major corrections. Despite the fact that some glass forming elements are excellent gel formers, there are even more exceptions. From a practical stand point, silicate glasses are still the most important group. In the sol–gel literature, SiO_2 is the most investigated system. Both glass and gel formation ability is excellent. Discrepancies appear with other elements, as indicated by the examples in table 1.

For glass formation by melt, the only way to obtain a glass is by cooling. Crystallisation depends on the cooling rate and nucleation and can be extremely slow. That means only a few parame-

Table 1

Element	Glass formation (oxide glasses)	Gel formation
Si	excellent	excellent
Ti	poor	excellent
B	good	poor
Zr	poor	excellent
Al	reasonable	good
Ge	good	good

ters exist, which are pretty well known and controllable in most cases. For gel formation, the chemical parameter besides the "gel-formation ability" defines strongly whether amorphous and homogeneous gels are obtained or not. For example the preparation of alumina gels according to Yoldas [16] leads to mainly crystalline boehmite type gels. Teichner [17] showed that alumina gels obtained by hypercritical drying are amorphous up to 600°C. In our own investigations (results to be published in detail later), we showed that high temperature stable amorphous alumina gels could be obtained by complex formation of alkoxides as precursors. But of course, no Al_2O_3 "glasses" can be obtained. This amorphous phase alumina was very helpful in the synthesis of homogeneous amorphous cordierite gels, too. The avoidance of crystallization of the different single phases during the gel formation is a prerequirement for synthesizing highly reactive multicomponent ceramic powders. This shows how strong the influence of change of chemical environment can be with respect to the properties of the synthesized gels. But the possibilities of chemistry are not exploited at all in this case.

TiO$_2$ is different: it is impossible to synthesize TiO$_2$ glasses, but it is easy to prepare amorphous titania gels, either in the form of monoliths [16] or powders [18]. It is not possible to obtain glasses from these gels, but, for example, within the system TiO$_2$/SiO$_2$ glasses from gels can be made much more easily than by melting. The preparation of TiO$_2$ gels can be influenced by chemistry, too: in the aqueous by change of pH value from acid to base, titanyl compounds such as $TiO(NO_3)_2$ can be precipitated as partially crystalline powders. The addition of water to Ti-alkoxides has the same effect. Gels can be obtained by controlled water addition to alkoxides (diluted e.g. with ethanol, by the CCC method [19], by the silica method [19], or by complexation of the Ti e.g. as described by Livage [20]). In the case of boron, Brinker [21] has shown that, depending on the state of coordination, boron can act as a gel former or not. This is similar to the glass chemistry of boron, but in opposition to this, the coordination state of boron can be influenced by wet chemistry during the sol–gel synthesis. Moreover,

the gel formation power of a given element is also influenced by the composition. Addition of ionic species e.g. in alumina gels can alter the surface charge and change the stability of sols, thus leading to the precipitation of different gel structures.

These few examples show that the gel formation process is only partly based on the ability of network formers to form a gel-like inorganic network. Of course, the ability to build up a three-dimensional network is an indispensable prerequisite. But how far this ability can be used for gel formation mainly depends on the applied chemistry. Again one can say, that the number of parameters is too great to allow systematic investigations of a representative number of systems. The main parameters are: the element, the solvent, reaction conditions (pH, T), composition, complex formers, sequence of the addition of different compounds, type of precursors.
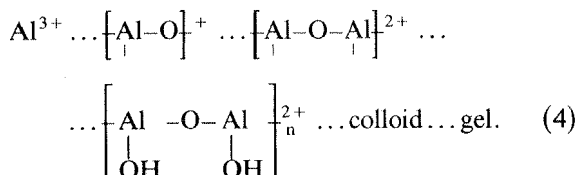
2.1.3. Precursors

There are only a few general requirements for sol–gel precursors. They have to be soluble in the reaction media and they have to be reactive enough to participate in the gel forming process. Therefore, especially the network forming components (monomers or colloids) have to be reacted into active forms *after* the preparation of a solution or a homogeneous colloidal sol (homogeneous in that case means a sol with particle sizes small enough to obtain suitable component distribution). For stable colloids (which in general remain stable due to the surface charge of their colloidal particles) the neutralization of surface charges (isoelectric point) leads to gelation, including the following basic reactions:

- neutralisation of surface charges,
- aggregation,
- further condensation by reactive surface groups,
- gelation (accompanied by a strong viscosity increase) to a solid gel.

Change of surface charge can easily be carried out by change of pH. Matijević [23] was able to prepare monodispersed ceramic powders by slowly changing the pH value versus the isoelectric point in different aqueous systems, e.g. alumina from the alumina sulphate. In this case, coming from the acid side, by raising the pH value, a slow

polymerisation of the alumina takes place, leading to gelation

$$Al^{3+} \ldots \left[Al{-}O\right]^{+} \ldots \left[Al{-}O{-}Al\right]^{2+} \ldots$$

$$\ldots \left[\begin{array}{cc} Al & -O- Al \\ | & | \\ OH & OH \end{array}\right]_n^{2+} \ldots colloid \ldots gel. \quad (4)$$

Livage used the well known chemistry of polyanion formation of several transition metals (e.g. V, W) to synthesize gels with interesting properties using this principle, but in this case applying high pH values [24]. These reactions can be carried out in aqueous solutions using common compounds as precursors (e.g. Al-sulphate, vanadates). But despite the fact that in the chemical literature (for example see textbooks of inorganic chemistry) much knowledge is gathered concerning the gel formation process of inorganic network formers, the knowledge in only a few cases is exploited for modern sol–gel material synthesis. Poor solubility of inorganic compounds in organic solvents is probably one of the main reasons.

The following can be used as precursors if soluble:

– salts: the role of the anion has to be taken into consideration; salts with anions that can easily be decomposed like nitrates, acetates, formiates are preferable; salts of network formers like $ZrO(NO_3)_2$ can be used, too;

– oxides: especially oxides of network modifiers e.g. Na or K are preferable;

– hydroxides;

– complexes: chelated precursors can be used on the basis of solubility reasons or in order to change the reactivity of the precursors, as demonstrated with Ti alkoxides [25,26].

– alkoxides, acylates, amines: alkoxides are the most common sol–gel precursors, since they are commercially available for the most important elements; due to the work of Bradley et al. [27] their basic chemistry is well known; acylates are commercially used in silicon glues; amines are used in the case of silicon in form of silazanes as Si_3N_4 precursors.

It is very difficult to predict the type of precursor to be used for a given aim. The reactivity of a

precursor does not only depend on its chemical nature but also on the applied reaction conditions. For example, for the formation of lead zirconium titanates it does not make any difference whether lead is introduced as nitrate, diacetate or tetraacetate [28]. The ceramic powders have identical densification and sintering behavior. This is mainly due to the very low decomposition temperature of these salts which lead to PbO formation at about 100–120 °C. The use of $Ba(NO_3)_2$ e.g. for $BaTiO_3$ ceramics leads to phase separation since $Ba(NO_3)_2$ crystals are formed which are stable up to several hundred degrees. Ba acetate decompose beginning at about 250 °C leading to finely divided $BaCO_3$ [29], which is highly reactive, thus leading to $BaTiO_3$ temperatures above 800 °C.

Another example will be given for the precursors: sodium boron silicate glasses can easily be made by hydrolysis and condensation of NaOR, $B(OR)_3$ and $Si(OR)_4$ (see scheme 1).

DSC analysis does not show a detectable difference between these different gels. This indicates that the network forming power of the Si is enough to build up a gel, independent of the precursors of the other components. This tells us that it might be worthwhile to investigate how far expensive alkoxide precursors can be substituted by cheaper ones in sol–gel processing, but now systematic rules can be given.

In conclusion, one can say that the question of the type of precursor has to be investigated for each system and for each set of reaction and processing parameters. Then chemistry is a very

$$NaOR + B(OR)_3 + Si(OR)_4 \xrightarrow[-HOR]{+H_2O}$$

$$Na_2O \cdot B_2O_3 \cdot SiO_2 \cdot aq$$
gel
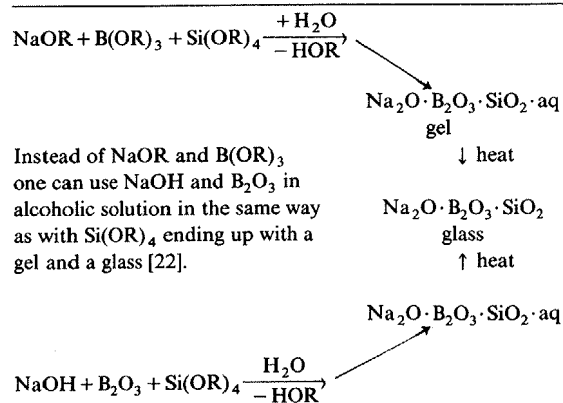
Instead of NaOR and $B(OR)_3$ one can use NaOH and B_2O_3 in alcoholic solution in the same way as with $Si(OR)_4$ ending up with a gel and a glass [22].

↓ heat

$$Na_2O \cdot B_2O_3 \cdot SiO_2$$
glass

↑ heat

$$Na_2O \cdot B_2O_3 \cdot SiO_2 \cdot aq$$

$$NaOH + B_2O_3 + Si(OR)_4 \xrightarrow[-HOR]{H_2O}$$

Scheme 1.

helpful means by which to optimize the material properties as well as the process economy.

2.1.4. Hydrolysis, condensation and homogeneity

As indicated above, different types of precursors can be chosen for sol–gel techniques: the common prerequisite for them is to be soluble in at least one solvent. Colloidal solutions are allowed but can lead to restrictions with respect to homogeneity. Therefore, the following considerations are mainly concerned with the hydrolysis of alkoxides. The hydrolysis reaction can be considered as a source for reactive monomers or oligomers. It seems to be a rule that *one* network former has to be introduced at least partially by a hydrolysable precursor, but sufficient investigations have not been carried out on this problem. Whether salts or soluble oxides can be used as precursors depends on the system; for Si containing compositions, in general Si esters have to be used, if the colloidal route (use of silica sols) is not possible. No simple monomeric soluble salts or oxides exist. Si esters do not have enough solubility to allow water to be used as solvent, and organic solvents have to be used. But for economic advantages, e.g. alkaline or earth alkaline components can be used as oxides, nitrates or acetates for sol–gel synthesis; a great deal of them are fairly soluble in alcohol.

Thermodynamic parameters can have various influences on the hydrolysis process. Important parameters are the solvent, temperature, complex ligands or pH value. Beside that, even the order of compound addition or the H_2O addition rate can be extremely important. This also relates to the question of homogeneity. Hydrolysis rate (since hydrolysis is the reactive monomer producing the reaction) is one of the most important steps with respect to sol and gel properties.

Homogeneity in a one-component system seems to be an unusual question, but it can be related to the distribution of voids within the solid material, e.g. pores filled with ligands or gases. The larger the pores are, the more inhomogeneous the material can be considered. Large pores decrease the densification or sintering rates of gels. Influencing parameters again are the type of precursor and the reaction conditions. In fig. 2 the
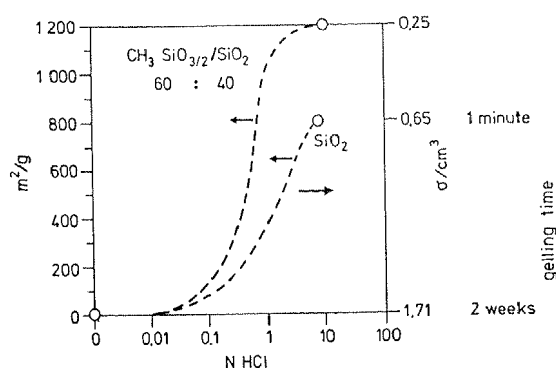

Fig. 2. Gelation, BET surface and densities of different gels depending on HCl concentration during hydrolysis and condensation.

influence of pH on the BET surface of SiO_2 gels from $Si(OR)_4$ is shown. Other relevant structural parameters like density or gelling time are given, too. In addition to this, the behavior of a two-component system ($CH_3SiO_{3/2}/SiO_2$, published in [30]) is shown. This will be discussed in section 5 in detail. The BET surface area from SiO_2 gel can be varied from 0 to about 600 m^2/g only by varying the concentration of the added HCl. The higher density with increasing gelation times indicates relaxation by network rearrangement.

In multicomponent systems not only microstructure can lead to inhomogeneities but also structural effects based on a non-random-like distribution of the different elements. The hydrolysis rate in general depends on the type of precursors and thus reactive monomers are produced at different rates. Since condensation in general cannot be separated from hydrolysis, the consumption rate of those reactive monomers by condensation can influence the production rate by equilibrium, too. On the other hand, the condensation rate is determined by the production rate of monomers. Scheme 2 indicates the connections between hydrolysis, condensation and rates.

One can easily conclude that, based only on the assumption of different rates, a large variety of polymeric structures can be built up. The number of different rate constants increases if reactive oligomers are taken into consideration. On the other hand, the complexity of these processes makes it clear that it is extremely difficult to
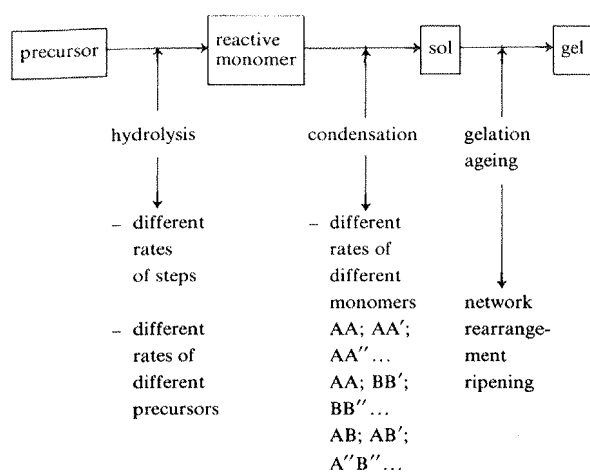
A...A''..: monomer A with different states of hydrolysis (e.g. A ≡
          SiOH(OR)₃...A'' ≡ Si(OH)₂(OR)

B: monomer B

Scheme 2.

analyse rates and structures to be built up in such multicomponent, three-dimensional networks.

As already indicated above, homogeneity of gels is very important for the further processing of material properties. A very convincing example is given by Mackenzie [31] who pointed out that a major advantage of the sol–gel process for the preparation of ceramic materials is the fact that sol–gel derived ceramic powders with random distributed components are closer to the desired final crystalline phase than a mixture of crystallites of this composition. As a consequence, the diffusion paths in the sol–gel system are in the range of nm, in the mixed oxide route in the range of μm (fig. 3). This can explain the observation that sol–gel powders very often show the better sintering behavior (lower temperatures).

In the case of glass compositions which, with a few exceptions are all based on silicate composition in the literature, the question of homogeneity does not seem to have the same importance as in ceramic systems. Due to the excellent gel (and network) forming properties of SiO_2, silicate based gels seem to be "homogeneous", if SiO_2 is the major network forming component. Thus, borosilicate gel or others can be prepared without major problems and seem to have roughly the

same properties as melted glasses. Differences might occur from different OH group contents or carbon contents. Another source of differences can be based on reactions during drying [32] including the mass transport of mobile ions like Na or K within the gel or to the surface.

In order to achieve maximum homogeneity the control of the network building rate of the different components is necessary. But up to now, no precise condensation kinetics in multicomponent systems have been established. For one component systems, most work is done for silica. Hydrolysis was investigated in addition to this in [33–38]. Kinetics data of other alkoxides are not available. Summarizing one can say that:

- better knowledge of hydrolysis and condensation kinetics in multicomponent systems would be very useful for homogeneity and related questions. But almost no data are available due to the complexity of the system and analytical problems.
- General rules can only be given for the siliceous acid esters in alcoholic solutions. This is only a very narrow aspect compared to the wide range and potential of sol–gel techniques.
- As a consequence systematic investigations should be done on the reaction chemistry of hydrolysis and condensation, especially in multicomponent systems, since they are of the main practical interest.
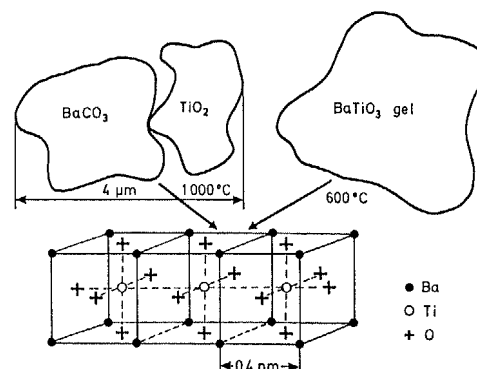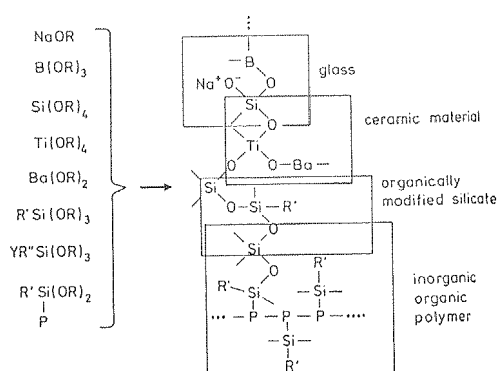- For sol–gel synthesis based on the present state-of-the-art, empirical chemical knowledge

Fig. 3. Comparison of BaTiO₃ formation from $TiO_2/BaCO_3$ with the gel method.

Scheme 3. Polymerizable ligand. In addition to the inorganic systems, the synthesis of inorganic–organic polymers is indicated, too.

has to be used for material development. The obvious disadvantage is the fact, that empirical knowledge in general is only related to the special case it has been developed for. The real difficulties may be demonstrated by the survey given in scheme 3 about the possibilities of sol–gel procedures, which exhibits the discrepancy between potential and fundamental knowledge.

In the following some practical results will be discussed. General possibilities to control rates of alkoxide reactions are:

– complex formation of precursors [24–27,38],
– controlled addition of water,
– controlled generation of water,
– controlled prehydrolysis of slowly reacting components [39],
– choice of the proper solvent.

Complex formation of acetates and acetylacetonates (acac) is well known from Ti compounds [27,20] such as alkoxides. The hydrolysis rate can be slowed down remarkably so that no precipitates appear and homogeneous sols and gels can be obtained according to LaCourse and Livage [25,26], this can be attributed to the complex formation including ligand exchange,
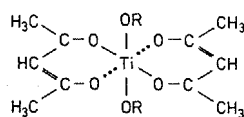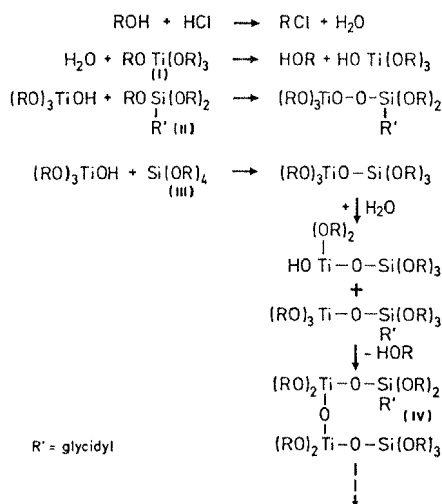

thus slowing down the attack of water. The reaction can be advantageously used for the equilibration of hydrolysis rates in combination with slowly reacting systems as $Si(OR)_4$. This can avoid phase separation and lead to better homogeneities. Our own investigations on Al(acac) complexes show that in this case it is not hydrolysis but condensation that is slowed down remarkably also leading to homogeneous, non-water sensitive stable sols. Prehydrolysis of slower reacting components seems to be an appropriate means by which to improve homogeneity according to refs. [39,40]. The interpretation is that in systems with a deficit of water, highly reactive $\equiv$MeOH groups exist, thus "immobilizing" the reactive component homogeneously into the network:

$$\equiv TiOR + HOSiO\equiv - \equiv Ti-O-Si\equiv \ + HOR. \quad (5)$$

This type of nucleophilic attack is enhanced by the increasing positive charge on the silica with an increasing number of OH groups as shown by comparison of $Si(OR)_4$ with $Si(OH)_4$. According to Henry and Livage [41] (based on electronic considerations), the condensation via $\equiv$Me–OR + HO–Me$\equiv$ is the preferred reaction. Our own investigations show that this can be used advantageously to overcome extremely different reaction rates especially in multicomponent systems, if water for hydrolysis is produced by homogeneous in situ reaction e.g. ester formation from an alcohol and an acid [19] (scheme 4).

Thus, for example, in mixtures of I:II:III = 30:50:20 it is possible to fix the titanium into a prepolymeric network (IV) by only generating about $\frac{1}{16}$ of the amount of water necessary for total hydrolysis by ester formation [40]. Direct addition of excess water to this prepolymer does not lead to any precipitates of $TiO_2 \cdot$ aq; no complex former is required. The effectiveness of this method has been proved for a variety of reactions. It is also of special interest for the use of Si esters with Si–C bonds, since those esters exhibit remarkably higher hydrolysis rates than unsubstituted ester [22]. Summarizing the situation of hydrolysis one can say that due to the fact that the number of reaction parameters it is still extremely difficult to *analyze mechanisms*. Valuable fundamental knowledge has been built up in the case of

$$ROH + HCl \longrightarrow RCl + H_2O$$

$$H_2O + RO\underset{(I)}{Ti(OR)_3} \longrightarrow HOR + HO\,Ti(OR)_3$$

$$(RO)_3TiOH + RO\underset{R'\,(II)}{Si(OR)_2} \longrightarrow (RO)_3\overset{}{Ti}O-O-\underset{R'}{Si(OR)_2}$$

$$(RO)_3TiOH + \underset{(III)}{Si(OR)_4} \longrightarrow (RO)_3TiO-Si(OR)_3$$

$$+\downarrow H_2O$$

$$\underset{HO\,\overset{|}{Ti}-O-Si(OR)_3}{(OR)_2}$$

$$+$$

$$(RO)_3\,\underset{R'}{Ti}-O-Si(OR)_3$$

$$\downarrow -HOR$$

$$(RO)_2\underset{\overset{|}{O}}{Ti}-O-\underset{R'}{Si(OR)_2}\;_{(IV)}$$

R' = glycidyl

$$(RO)_2\overset{|}{Ti}-O-Si(OR)_3$$

$$\downarrow$$

Scheme 4.

Si by NMR, GC and SAXS. On Al, first data became available only recently [42]. The problems are increased by the fact that, especially for highly reactive components, (such as alkaline, earth alkaline, boron, aluminum, zirconium and titania alkoxides and substituted siliceous esters) more difficulties arise by use of the common analytical tools, the same is true for multicomponent systems. Hopeful means for *material synthesis* are to control hydrolysis (and condensation) by complex chemistry and reaction rate control. Systematic investigation on solvent influence should be enhanced, too. Better analytical tools are necessary.

Condensation cannot be separated in many cases from hydrolysis. The condensation step is the most important step with respect to the structure of the synthesized polymer and its processing properties. Structural varieties in a given bulk composition can sometimes be eliminated by high temperature treatment which equilibrates structural differences. In other cases (e.g. phase separation in sols for thin films, incorporation of organics) these differences cannot be eliminated and lead to differences in material properties. The ideal case that condensation leads to a random distribution of elements (e.g. in multicomponent systems, is a purely theoretical one; due to the differences in chemical nature and reactivity, the systems try to reach their thermodynamically most

stable state and this, as a rule, is *not* the random distributed amorphous state.

The condensation reaction as well as the hydrolysis is a nucleophilic substitution type reaction. As through hydrolysis, the activity of the reaction center changes with increasing change of substituted ligands. Since there is a change to receive thermodynamic metastable or kinetically stabilized intermediates, structures can be influenced by parameters. As pointed out by Sakka [43], e.g. $Si(OEt)_4$ hydrolyses and condenses under special acid conditions to linear type of polymers

$$\begin{bmatrix} OR \\ | \\ -Si-O- \\ | \\ OR \end{bmatrix}_n ,$$
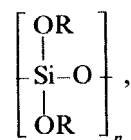
which can be used for fiber drawing. In base-catalysed systems, a branched growth mechanism takes place. First hints show that with other alkoxides similar effects may be possible, but there is a lack of systematic data [44]. More difficulties can be expected with multicomponent systems.

One of the major problems of material synthesis with sol–gel techniques is to obtain gels with a high oxide content (high density), because the shrinkage during densification should be kept as low as possible to avoid serious problems. The different surface areas and densities in fig. 3 indicate the strong influence of reaction conditions on structure during condensation. With respect to multicomponent systems different reaction rates can lead to the intrinsic inhomogeneity of the system, causing serious differences in reactivities for densifying or sintering. Especially with regard to crystallizing systems, phase separation in the gel state can lead to different crystalline phases in the crystallized product. GeO_2/SiO_2 systems do not form homogeneous amorphous products and cannot be transformed into glasses according to [45], if cohydrolysis and cocondensation are performed with ammonia from alkoxides. This points out again that homogeneous gels have to be obtained for further processing. Since there are no direct means for detecting molecular distributions, questions of homogeneity have to be answered by indirect means like material properties (optical, X-ray scattering or STEM analysis). There are no

general rules for obtaining optimal homogeneities. But the chemical variations described in section 2.1 can help to optimize homogeneity.

3. Drying, ageing, processing

The role of chemistry for the steps after gelation may not look very important but there are some interesting aspects especially with respect to homogeneity and purity. Drying in general is connected with shrinking. Zarzycki [46], Brinker and coworkers [47,48] have investigated the mechanisms very thoroughly on SiO_2-gels and glasses. They pointed out the fact that strains appear during drying, which can be calculated for different systems. If the strains cannot be stopped by relaxation, cracks appear and it will be difficult to obtain monoliths [49]. The strains are based on the fact that gels prepared by the sol–gel process are diphasic solids with pores filled with liquids. The liquid is removed from pores during drying. The liquid phase concentration gradient (driving force for liquid transport) leads to surface tensile stress and cracks begin to propagate from the surface, a very common observation during gel drying. Since the chemical (or physical) interaction of liquids with the pore walls is one of main causes of the capillary forces and the stress formation, it should be reduced. The main interaction is based on the pore wall OH groups, forming hydrogen bonds with water. The interaction depends on

- pore size: small pores are more efficient for interactions than large ones,
- temperature: increases diffusion without increasing capillary forces,
- chemical state of pore walls: number of OH groups or number of other hydrophilic groups,
- pore shape and interconnection: e.g. cylindric shape, bottle necks,

Network stiffness acts to prevent relaxation. The resulting shrinkage behavior exhibits the compromise of the material between its mechanical stability, its relaxation capability and the capillary forces.

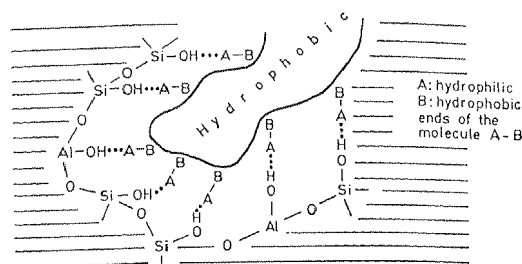For the reduction of the capillary forces, the

Fig. 4. Effect of bipolar molecules on pore wall properties.

interaction between the liquid and pore walls can be reduced by several means.

Bifunctional additives can be used, acting as pore wall surfactants and thus reducing liquid–pore wall interaction forces (fig. 4). Hench's DCCA may act at least partially in this way [50].

Another possibility e.g. with SiO_2 containing gel compositions, is to incorporate by hydrophobic organic groupings, direct bonds to the Si atom (e.g. from $CH_3Si(OR)_3$ as a precursor). As described in [51] the H_2O adsorption of porous gels can be reduced remarkably (fig. 5) and monoliths are much easier to obtain [19].

Other chemical reactions may occur during drying, like the transport of alkalines [32]; this can lead to carbonate formation, if transported to the surface and affects homogeneity strongly. Carbonate formation can also occur during the baking out of organics by oxidation. If earth alkalines (for example Ba) are present, serious complications may be the result. $BaCO_3$ is a very

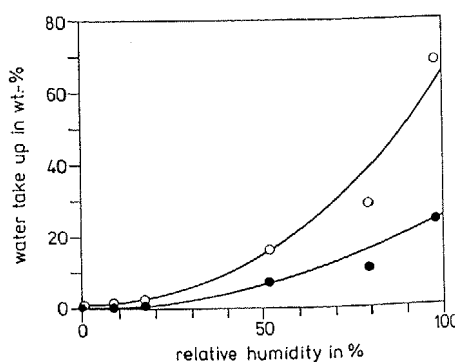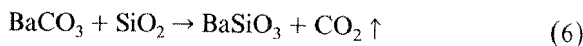Fig. 5. Effect of incorporation of $Si(CH_2)_2CH_3$ groups into amino group containing hydrophilic gels [19].

stable carbonate and can be decomposed at temperatures around $1200\,^\circ C$. Thermodynamics fortunately can be influenced by SiO_2,

$$BaCO_3 + SiO_2 \rightarrow BaSiO_3 + CO_2 \uparrow \qquad (6)$$

but despite this, carbonate formation should be avoided in these cases by removing the majority of organics before oxidation takes place (e.g. completion of hydrolysis, washing, vacuum evaporation).

4. Role of organics

Organics in sol–gel processes may play different roles. Concerning precursors, the organic groupings of alkoxides lead to solubility in organic solvents and prevent polymerisation in most cases (exception: transition metal methoxides [27]) and for a couple of systems, it is convenient to use liquid "inorganic" monomers. The organic groups in general are removed during hydrolysis, but very often not completely, and this can cause problems (e.g. carbon formation by pyrolysis). Non-hydrolysable organic groupings linked to network formers in any case reduce network connectivity and with respect to relaxation they act like $\equiv$MeOR groups. Other organics simply added to the sol as organic oligomeric compounds, can create similar effects. A general idea may be to incorporate organics like this in order to increase the network relaxation ability and to eliminate them, if desired by a thermal treatment. An additional effect may be the described reduction of interaction between water and the pore walls thus reducing the capillary forces and stress during drying and densification. Our results show that in the system $Na_2O/Al_2O_3/SiO_2 (10:20:70)$ SiO_2 can be introduced as $(C_6H_5)_2Si(OH)_2$. Thereby, the fourfold binding SiO_2 units are reduced to a twofold building unit, reducing network connectivity remarkably. This leads to a thermoplastic polymer which very easily forms a monolithic ceramic at $600\,^\circ C$ without cracking [52]. This indicates that the major disadvantages of sol–gel processing can be overcome in some cases by *inorganic–organic processing* (IOP) but not many investigations have been carried out in this field up to now.

Further investigations show that IOP also works with Si bond epoxide or methacrylate groupings. One interpretation might be that the relaxation behavior of organically modified systems can lead to a solvent-free, dense network under modest thermal conditions (100 to $200\,^\circ C$). Homogeneously distributed organics can be baked out under controlled conditions and the remaining porosity (voids from oxidized organics) is ideal for further densification.

5. Incorporation of organics

The use of organic network formers or organic network modifiers leads to typical inorganic–organic hybrid materials with inorganic backbones [19]. A large variety of reactions is possible to introduce different modifiers such as amino-, carboxy-, cyano-, aldehyde-, olefin-, epoxy-, or olefinic groupings [53]. Polymerizable ligands together with polymerizable monomers can lead to materials with inorganic and organic polymeric networks according to scheme 5, including coordination polymers by complexation. This type of chemistry is characterized by two different (and mainly independent) steps: the sol–gel processing to the inorganic network and the organic processing. The sol–gel process can be influenced by the organic grouping:
- by steric reasons,
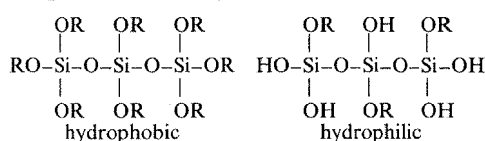- by reactivity reasons of the siliceous ester,
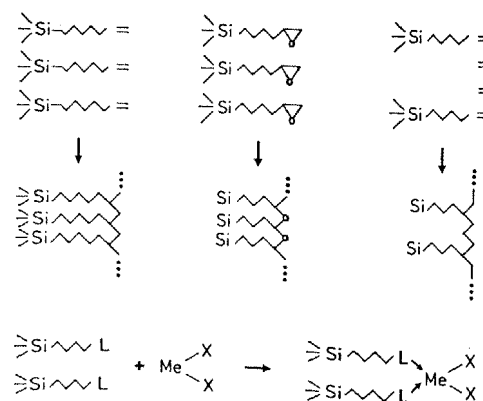
Scheme 5.

- by the reactivity of the organic grouping,
- by reduced network connectivity,
- by different densifying behavior.

It is of great importance to link the organic grouping carrying units in an early stage of condensation to the inorganic backbone in order to avoid phase separation, e.g., due to a difference of hydrophilicity of the two backbones.

Oligomers can be hydrophobic as well as hydrophilic according to their number of OH groups:

$$
\begin{array}{cc}
\begin{array}{ccc}
OR & OR & OR \\
| & | & | \\
RO-Si-O-Si-O-Si-OR \\
| & | & | \\
OR & OR & OR \\
\text{hydrophobic}
\end{array}
&
\begin{array}{ccc}
OR & OH & OR \\
| & | & | \\
HO-Si-O-Si-O-Si-OH \\
| & | & | \\
OH & OR & OH \\
\text{hydrophilic}
\end{array}
\end{array}
$$

That means the reactivities of the alkoxides with respect to hydrolysis and condensation have to be adapted for this type of synthesis. Olefinic polymerization e.g. can be initiated by common types of initiators.

Polymerization of silane linked epoxides can also be influenced by sol–gel reaction conditions [54], by H_2O addition to glycols [55]. This can be avoided by chemical means, such as a proper choice of polymerisation catalysts and reaction conditions [56]. Recent investigations show that sol–gel techniques can be used to reinforce organic polymers [57,58] by creating finely dispersed phases or interpenetrating networks. These new classes of inorganic–organic hybrid materials are at an initial phase, but seem to have a high application potential. The basic chemistry is just being explored now.

6. Conclusions

Chemistry plays an important role for the sol–gel process. It is complex and in most cases it is difficult to evaluate mechanisms. It seems to be very difficult to separate the reactivities of single components, especially with respect to multicomponent systems, but these systems are very often of highly practical interest. Chemistry has to help to find out the important parameters for material tailoring. Progress in this field has to be based on interdisciplinary research by the cooperation of chemists and material scientists. This "new"

chemistry also involves the possibility of incorporating organics into inorganic networks, a class of material which is just now becoming of interest for many applications.

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