CHEMICAL PROCESSING UP TO GELATION

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ABSTRACT

The sol-gel process up to gelation is governed by the rules of chemistry. In case of homogeneous solutions, investigations on kinetics and structures can be carried out by common means of instrumental analysis. Once the system becomes colloidal or solid, indirect means for structural analysis have to be used. Numerous investigations show that material properties can change drastically as a function of changing reaction parameters. This is attributed to the structure forming steps during condensation. As consequence of a lack of simple structure revealing methods and a huge number of variation parameters not too much knowledge exists about structure (of sols) to material properties relations. The main influencing parameters are quite well-known, their applicability for a special system has to be investigated for each case.

1. INTRODUCTION

The chemical synthesis of inorganic materials has become an important principle in materials science. Despite the fact that the basic reactions are well known from nature (e.g. agate and chalcedon formation) and chemistry (e.g. Ebelmen found in 1844 that SiO_2 can be obtained from the hydrolysis of $Si(OC_2H_5)_n$; alumina is obtained by the hydrolysis and condensation of aluminates by the Bayer process; SiO_2 is produced from water glass by condensation), these reaction principles only have 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 investigations have spread out dramatically. Thus, it is almost impossible to review the important literature in a comprehensive article. A good survey over the state of art can be received from the congress 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 herein. The history tells us that two research fields, namely chemistry and material science have to be combined in order to have a good progress.

Basically the sol-gel process means the synthesis of an inorganic network by a chemical reaction in solution at low temperature. 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 acqueous system, but aqueous reactions like these are known since a very long time.

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 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 done by 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. Equation (2) shows the most important condensation reactions: The condensation of two M-OH groups or the reaction of an M-X with a M-OH group.

$$\equiv M{-}X + H_2O \longrightarrow \equiv M{-}OH + HX \qquad (1)$$

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

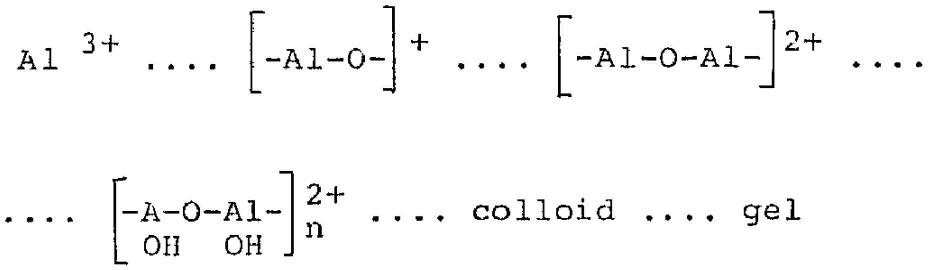
$$\begin{aligned} \equiv M{-}OH + X{-}M\equiv &\longrightarrow \equiv M{-}O{-}M\equiv + HX \\ \equiv M{-}OH + HO{-}M\equiv &\longrightarrow \equiv M{-}O{-}M\equiv + H_2O \end{aligned} \qquad (2)$$

The chemistry of processes like this should be more easily to be 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 better spoken, 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 (1).

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 <u>after</u> 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 easily can be carried out by change of pH. Matijević[12] 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 sulfate. In this case, coming from the acid side, by rising the pH value, a slow polymerisation of the alumina takes place, leading to gelation (3)



$$\mathrm{Al}^{3+}\ \ldots\ \left[\text{-Al-O-}\right]^{+}\ \ldots\ \left[\text{-Al-O-Al-}\right]^{2+}\ \ldots \qquad (3)$$

$$\ldots\ \left[\begin{array}{c}\text{-A-O-Al-}\\ \text{OH}\quad\text{OH}\end{array}\right]^{2+}_{n}\ \ldots\ \text{colloid}\ \ldots\ \text{gel}$$

Livage used the well known chemistry of polyanion formation of several transition metals (e.g. V, W) to synthesize gels with interesting properties by this principle but in this case coming from high pH values[13]. These reactions can be carried out in aqueous solutions using common compounds as precursors (e.g. Al-sulfate, vanadates).

But despite the fact that in the chemical literature (for example see text books 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 probably is one of the main reasons.

As precursors can be used if soluble:

- salts: the role of the anion has to be taken into consideration; salts with anions easily to 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 from solubility reasons or in order to change the reactivity of the precursors, as demonstrated with Ti alkoxides[14,15)

- 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, Mehrotra and coworkers[16) 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[17)]. 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 as precursor decomposes at about 250 °C leading to finely devided $BaCO_3$[18)] which is highly reactive thus leading to $BaTiO_3$ at temperatures above 800 °C.

Sodium boron silicate glasses can easily be made by hydrolysis and condensation of NaOR, $B(OR)_3$ and $Si(OR)_4$, but NaOR and $B(OR)_3$ can be substituted by NaOH and B_2O_3 without problems.

DSC analysis does not show a detectable difference between these different gels. This indicates, that the network forming power of the Si is high enough to build up a gel, independent on 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 type of precursor has to be investigated for each system and for each set of reaction and processing parameters. Then chemistry is a very helpful mean to optimize the material properties as well as the process economy.

2. THE DIFFERENT REACTION STEPS

Due to the high numbers of variables, the process starting from monomers and ending up in highly threecross-linked solids is a very complex one. This is responsible for the more or less poor knowledge about structures to be developed and reaction mechanisms. Two main regimes can be distinguished. The "homogeneous" or "molecular" regime, which is characterized by a homogeneous liquid phase with dissolved small molecules and which can be investigated by structure and size sensitive methods used in molecular chemistry and a second regime, the heterogeneous (or multiphasic) polymeric regime, where indirect methods like scattering methods (e.g. X-Ray, neutron, mechanical properties) have to be used for analysis.

Between these two regimes, a transition state exists, which can be described as a colloidal state. Whereas the molecular and the colloidal state are defined as the "sol" state, the polymerized multiphasic state is defined as the "gel" state. The transition from the sol to the gel state can be achieved by three different ways:

- growth of polymeric molecules (which crosslink randomly to a three dimensional network)
- growth of individual particles (which grow together as they become larger)
- stabilisation of colloids by surface charges (change of the zeta potential and a following interparticular condensation process leads to gelation).

As long as the reaction takes place in a homogeneous solution, it can be followed by structure relevant analytical methods like spectroscopy (IR, NIR, UV, NMR), gas chromatography, mass spectroscopy or others. For molecular size determination, approbriate methods like light scattering determination of the rheological behavior or vapor pressure depression can be used. From this, informations about structure and size of small molecules and kinetical data can be obtained. Due to the tremendous number of parameters numerous reaction paths are existing. Main influencing parameters are:

- precursors (e.g. salts, oxides, alkoxides, complexes, colloids)

- reaction conditions (solvents, temperature, catalysts, pH)

- mechanical parameters (e.g. stirring, refluxing, ultrasonic treatment).

Molecular precursors require an activation reaction to be transformed into species ready to perform a condensation reaction. In most cases, this reaction is a hydrolysis raction (4):

$$\begin{aligned} &AlCl_3 \xrightarrow{+H_2O} Al(OH)_3 \\ &Si(OC_2H_5)_4 \xrightarrow[-C_2H_5OH]{+H_2O} Si(OH)_4 \end{aligned} \qquad (4)$$

This simple looking reaction is very complex, if one starts to look into details: The hydrolysis rates with exception of Si-esters are very quick and no data about rates are available.

As general rules, one can say the hydrolysis rate increases with:

- increasing polarity of the Me-X bond
- with decreasing stabilization of the solvatation or complex forming effect of solvents or complex formers
- with increasing concentration of catalysts, e.g. acids or bases
- with temperature.

It decreases, especially if alkoxides are used with:

- increasing chain length of the alkyl chain
- use of complex formers (e.g. ß-diketonate complex of Ti alkoxides).

For example, it is possible to stabilize intermediates by complex formation, e.g. partially hydrolyzed Al alkoxides[19)].

The best investigated systems with respect to hydrolysis are $Si(OR)_4$ systems, since rates convenient to be measured by NMR or IR can be chosen by the concentration of protons or OH groups as catalysts. The reaction rate is a superposition of at least the individual rates of the hydrolysis of $Si(OR)_4$ (I), $HOSi(OR)_3$ (II), $(HO)_2Si(OR)_2$ (III), and $(HO)_3SiOR$ (IV). The k_i are increasing from I to IV[20)]. Substitution of a $\equiv$Si-O-R bond by a $\equiv$Si-C$\equiv$ bond in the precursor increases the H^+ and decreases the OH^- catalysed rate[21)]. One has to take into consideration, that very often alkoxides are oligomeric species showing different rates than the monomeric ones[16,22,23)]. The relevance of the detailed knowledge on the influence of type of precursor and reaction conditions on the material properties can be easily demonstrated by Al_2O_3 as an example. It is possible to receive crystalline intermediates (e.g. boehmite or bayerite) by hydrolysis of $Al(i\text{-}prop)_3$ at $t \leqq$ 100 °C[24] on the one hand, which undergo several instable crystalline phases on their way to α-Al_2O_3 and one can prepare amorphous phases by complex formation with ß-diketonates, stable up to 800 °C which change directly to α-Al_2O_3 without having seen other crystalline intermediates[25]. This indicates the strong influence of structure relevant parameters during chemical synthesis.

Another example for property tailoring by chemistry is the synthesis of ceramic powders with special properties. K. Bowen, E. Matijević and their coworkers have shown how to prepare monosized powders from solution[26,12]. By Rinn et al.[27] it was shown, that the size of ZrO_2 powders exactly could be controlled by complex formation. Strehlow[28] developed a model for the stability of monosized spherical particles in solution as a function of solubility of monomers and oligomers and the surface characteristics of the particles. Naß et al.[19] could show, how complex formers influence the formation of Al_2O_3 precursors, and similar work was carried aout by Livage and LaCourse on titania[14,15]. One can see that chemical parameters are playing an extremely important role for property tailoring. A survey over the most important influences is given in table 1.

Another very important field of chemistry together with sol-gel processing is the introduction of organics into sols and gels.

Organics in sol-gel processes may play different roles[29]. Concerning precursors, the organic groupings

Table 1. Influences of chemistry related parameters and sol-gel properties.

Parameter	Affected properties
precursors	kinetics; structure of oligomers; distribution of components
solvent	kinetics; conformation of precursors; gelation point (solubility of oligomers)
temperature	kinetics; growth reaction (structure of polymers (crystalline, non-crystalline) solubility (gelation point)
catalysts	kinetics (precursor dependant; in multicomponent system different effects on different precursors); distribution of components
pH	catalytic effect of H^+ and OH^-; isoelectric point (gelation); kinetics; structure of polymers; stability of sols
additives	complex formers kinetics; solubility; structure and properties of sols; structure of gels; gelation point; rheology
	tensides surface chemistry of colloids; agglomeration; processing properties of fine particles; rheology
mechanical parameters	stirring gelation point; particle size; agglomeration
	ultrasonic treatment miscibility; solid content of sols; processing of sols; distribution of components

of alkoxides lead to solubility in organic solvents and prevents polymerisation in most cases (exception: transition metal methoxides 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 ≡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 reduction of interaction between water and the pore walls thus reducing the capillary forces and stress during drying and densifying. Own 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 reduced to a twofold building unit, reducing network connectivity remarkably. This leads to a thermoplastic polymer which forms a monolithic ceramic at 600 °C very easily without cracking30). This indicates that major disadvantages of sol-gel processing can be overcome in some cases by <u>inorganic-organic processing</u> (IOP) but not much investigations are carried out in this field up to now.

Further investigations show that IOP works with Si bond epoxide or methacrylate groupings, too. 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 °C). Homogeneous distributed organics can be baked out under controlled conditions and the remaining porosity (voids from oxidized organics) is ideal for further densification.

3. CONCLUSIONS

Chemistry plays an important role for the sol-gel process. It is complex and in most cases it is difficult to evaluate mechanisms. Especially with respect to multicomponent systems it seems to be very difficult to separate reactivities of single components 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 cooperation of chemists and material scientists. This "new" chemistry also involves the possibility of incorporating organics into inorganic networks, a class of material which just now becomes of interest for many applications.

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