The Sol-Gel Process for Non-Metallic Inorganic Materials

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1. Introduction

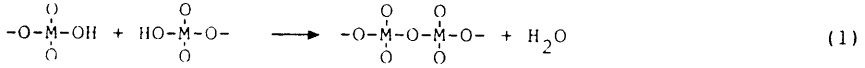
This paper will give an overview over the potential and some special aspects of the sol-gel process. The sol-gel process has gained interest in industry as well as in the scientific field during the last 20 years. In general, the process describes the transition of a system from a liquid (mostly colloidal) into a solid (gel) phase. The gel phase may be defined according to P. Flory as at least diphasic where one phase is solid and where two phases are interpenetrating. The high interest in most cases results from the possibility of synthesizing non-metallic inorganic materials like glasses, glass ceramics or ceramic materials, at low temperatures compared to the high-temperature process required by glass melting or firing. In the past, a lot of work was carried out in order to investigate the potential of the process, the mechanisms and industrial applications. This work was carried out mainly from the materials science point of view in order to synthesize materials with special properties or to be able to use new and advantageous techniques. It could be shown that with different techniques it is possible to vary the composition of the synthesized materials over a wide range of the periodic system of elements [1 - 10]. Table 1 illustrates the num-

Table 1 Overview over the elements used as components in the sol-gel process according to [11]

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H																2 He
3 Li	4 Be										5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 a) (Ung)	105 b) (Unp)													

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

ber of elements used in the sol-gel process according to DISLICH [11]. In order to produce fairly homogeneous solids, network-forming components have to be present to build up a three-dimensional network during the chemical reaction described as the network-forming step and which in general is a condensation reaction (eq. 1).



(1)

Lower-valent compounds can be incorporated into such a network, but it depends very strongly on composition and reaction conditions whether homogeneous solids are obtained or not. The condensation process generally leads to an amorphous product, since the three-dimensional cross-linking in the liquid phase of the network formers prevents crystallization during the sol-gel transition in most cases. To produce amorphous solids seems to be desirable for various applications: For glasses it is a prerequirement. If not, very high temperatures would have to be applied afterwards which would wipe out the whole low-temperature processing advantage. For ceramic materials where the crystalline phase is defined by thermodynamics as a function of temperature, an amorphous state can lead to high reactivity precursors and thus allows us to apply lower firing temperatures as usual. Beside the low processing temperatures, other advantages can result from the sol-gel method: Homogeneous incorporation of doping components by liquid mixing; preparation of adjustable intermediate properties like rheology for coating or spinning procedures; high purity by easy purification of starting components; preparation of glasses with unusual compositions by avoiding high-temperature rapid crystallisation ranges; incorporation of organic components into an inorganic network.

2. Some Aspects of Mechanisms of Hydrolysis and Condensation of Simple Systems

The reaction path from the liquid to the solid system can start from two basically different starting systems. One can use stabilized aqueous sols and perform the condensation step by sol destabilization (fig.1).

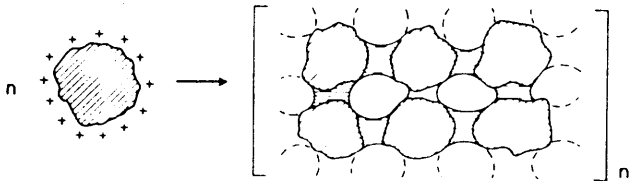
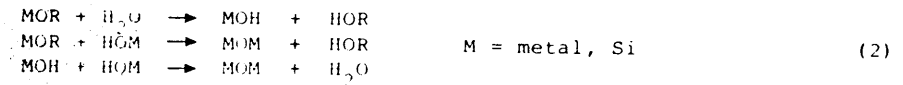


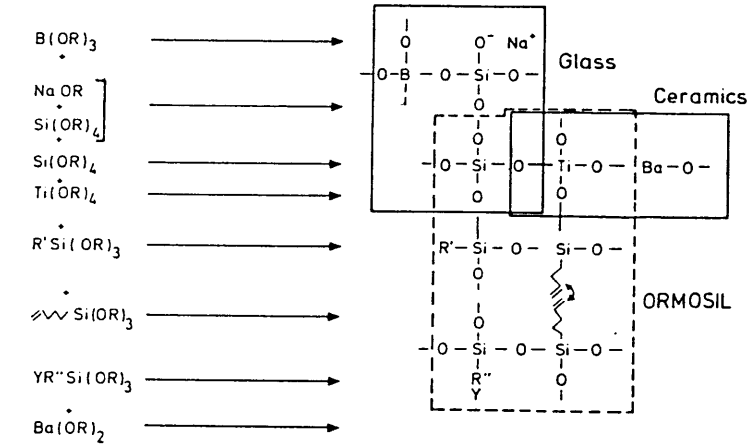
Fig.1 Sol destabilization by colloid discharging; ≡ = neck forming zones

The other, most common possibility is the hydrolysis of organometallic precursors and subsequent condensation (eq. 2).



(2)

In principle, the prototype of this reaction, the hydrolysis and condensation of silicon alkoxides has been known for quite a while and was discovered by EBELMEN in 1844 and published in 1846 [12]. Since most of the alkoxides are very sensitive to water, reaction (1) can be carried out with a big variety of compounds. In combination with the metalorganic reaction path, organic network formers or modifiers can be introduced by use of organically substituted silicoesters as starting compounds ($R'_n Si(OR)_{4-n}$) where R' is an organofunctional and OR a hydrolyzable grouping. The reaction scheme in eq. (3) shows the general possibilities of the metalorganic path for the synthesis of glasses, ceramic materials and organically modified silicates (ORMOSILs). Especially by the work of BRADLEY, MEHROTRA et al. [13], a lot of various metal alkoxides became available, so that the alkoxide way can be carried out with a big number of components.



(3)

The reaction path from a monomeric starting component to an amorphous solid includes several reaction steps as shown in figure 2.

The whole reaction path is complex, since the single steps are overlapping. The single steps are complex, too, as one can illustrate with the one-component system, silica. Silicoesters like tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) can be easily hydrolysed, and silica gels can be obtained. The majority of the mechanistical investigations are carried out with these systems. The simple-looking step of hydrolysis turns out to be very complex, since it can be influenced by numerous reaction parameters (T, type and concentration of catalyst, amount and concentration of water, solvent), and since the reaction is a 4-step reaction (4 hydrolysable groups).

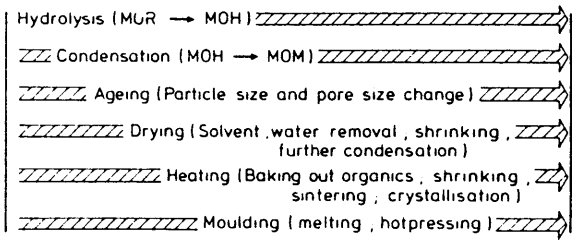


Fig.2 Scheme of reaction steps in the sol-gel process

Different attempts were made to evaluate the mechanism, but up to now no fully proved mechanism exists [14-22]. Some general conclusions can be drawn: Hydrolysis of orthoesters can be catalysed by acids and bases; it is a nucleophilic substitution reaction, probably of the SN_2 type. Despite different attempts, the overall reaction cannot be described by a simple reaction order since the single reaction steps may show different rate constants [22]. The reaction is an equilibrium reaction, that means with alkohol present, ≡SiOR groups remain within the gel. For the future it seems to be possible to receive more information on the hydrolysis reaction with modern analytical tools (NMR, IR, NIR, MS). The condensation reaction is even more complicated, because a molecular analysis of the growing chain or the quantitative analysis of the particle growth steps are almost impossible. But both, hydrolysis and condensation, are the main steps defining the structure of the growing and the final polymer. The structure after being built up can be affected by the following processing steps, but it is primarily fixed by the condensation chemistry. Up to now one has to apply experimental experience in order to tailor material properties by choice of reaction conditions. YOLDAS could clearly show how immense structural effects can influence the material behaviour as a result of change of reaction conditions with $Al(OH)_3$ gels as an example [23]. Some general results should be mentioned: Acid and base catalysis have different effects on the ratio between hydrolysis and condensation velocity. Whereas in the case of acid catalysis the condensation reaction tends to start at a pretty late stage (except at very low pH values) with bases as catalysts, condensation starts relatively early [17, 24] (fig.3).

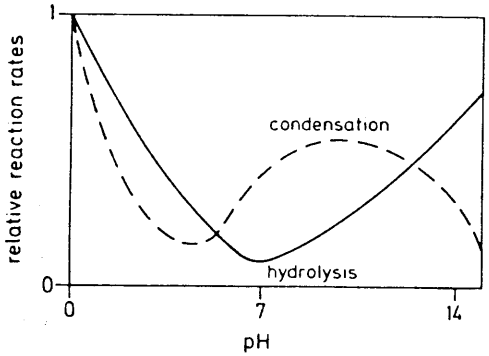


Fig.3 Hydrolysis and condensation of TEOS as a function of pH, according to [17]

The acid catalysis leads to a more polymeric type of gel with linear chains as intermediates [18]. Then gelation occurs by crosslinking. Base catalysis leads to so-called colloidal gels [25]. Gelation occurs by cross-linking of the colloidal particles according to eq. (1). One can conclude from these results that hydrolysis and condensation conditions define the primary structure of the gels which influence strongly the further steps. Since these steps include chemical reactions, it is necessary to evaluate the chemical mechanisms and to take into account all parameters which will influence these reactions. This is the prerequirement for receiving reproducible results and for tailoring properties.

3. Problem of Monolithicity

If highly cross-linking units are used as network formers, a three-dimensional network will be formed in solution which will be a true gel according to the definition mentioned above. The liquid phase is in the pores of the solid skeleton. In order to get dense products it is necessary to eliminate the pores. Strong attempts have been made in order to get large pieces of material from gels without the application of hot pressing [26, 27]. But it is very difficult, since during drying a remarkable shrinkage takes place. The shrinkage is caused mainly by capillary forces of the liquid within the pores. Since the liquid transport to the gel surface requires a concentration gradient a density gradient follows which causes stress and this mostly leads to cracks within the monolith. The problem can be partially overcome by very long drying times (low gradients) or the application of higher drying temperature combined with higher vapor pressures. According to ILER [28] and references therein the following means (table 2) can help to receive gel monoliths by keeping up the origin liquid derived low-density gel structure.

Table 2 Means to receive monolithic porous dry gels

1. Strengthening the gel by reinforcement, increasing the strength of the interparticle bonds (opposing shrinkage forces);
2. Reducing surface tension forces by enlarging pore diameter by an ageing (liquid phase) or hydrothermal process;
3. Replacing water with a polar liquid of lower surface tension, for example water by alcohol;
4. Making the surface hydrophobic;
5. Heating the liquid-filled gel under pressure above the critical point where no liquid-vapor boundary exists ("aerogel process").

The drying and shrinking process was investigated by ZARZYCKI and coworkers very closely [29-31]. Our own investigations show that with hydrophobic components like the $CH_3SiO_{3/2}$ group, high porosity products with specific surface areas up to 1200 m^2/g can be obtained by simple variation of the pH and without applying the other means listed in table 2 (fig.4).

Thereby, despite increasing amounts of network modifiers which should lead to lower specific surface areas, the specific surface area increases, caused by increasing hydrophobicity. The hydrophobicity causes an additional effect: The water vapour adsorption is reduced drastically, as shown in fig.5. That might be very important for applications of porous materials.

ZARZYCKI could show that it is comparatively simple to produce monolithic glass once monolithic dry gels are obtained [29]. In later investigations he could show that the aerogel process can be extended to multicomponent systems, too [32].

Techniques for the preparation of aerogels by the sol-gel process have existed for a long time. In 1932, KISTLER was the first who used the hypercritical aerogel process [33]. In the following period a lot of investigations were carried out to improve procedures and to find applications. An interesting result is reported by MARSHALL [34] who compared the packing density of a silica alcosol with that of the obtained aerogel, and found out that the densities are almost the same.

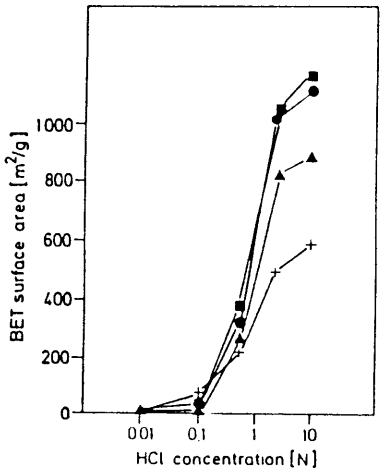


Fig.4 Specific surface area of $CH_3SiO_{3/2}/SiO_2$ cocondensates as a function of pH; + = silica; ▲ = 20, ● = 40; ■ = 60 mole-% of $CH_3SiO_{3/2}$

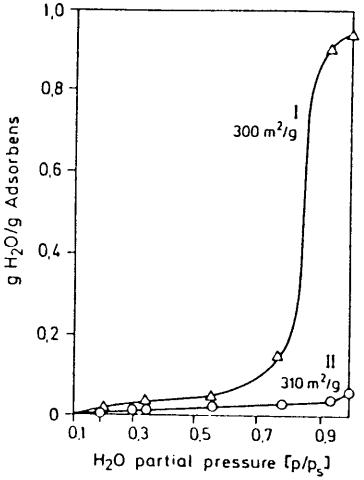


Fig.5 Water vapor room temperature absorption isotherms on two different gels; I = amino group containing gel (hydrophilic); II = methyl group containing gel (hydrophobic)

In these days high-porous, especially transparent materials gain more and more interest for different reasons, e.g. thermal isolation. That means, the sol-gel process, mainly used in order to obtain dense materials, in addition to this must be considered under the new objective to develop highly-porous materials. As mentioned above, up to now a big variety of components has been used in the classical sol-gel process. Investigations in order to receive highly porous materials with different components are an exception, and this opens a new field of sol-gel applications.

4. Further Aspects of the Sol-Gel Process

As mentioned above, the sol-gel process is based on network-forming components which build up an inorganic network during a polycondensation process. The network can be modified e.g. by low-valent cations, so-called network modifiers. The network modifiers decrease the bond strengthening in the sense of a decreasing network stiffness, which should lead to lower porosities. Figure 6 shows the surface area behaviour of two porous gels according to [35, 36] with different amounts of inorganic and organic network modifiers. The effect on temperature stability is also shown. A drop of specific surface area can be observed if increasing amounts of linear crosslinking network modifiers of the type $(CH_3)_2SiO$ and alkali ions are used (fig. 6a and 6b). In fig. 6b the two-dimensional units, despite their hydrophobicity, lead to denser materials.

The introduction of modifiers changes the physical and chemical properties of the material as well as the introduction of other network formers like Ti, Zr, Al. Only a few investigations on aerogels with other network formers or modifiers are known [32, 37]. It is a task of the future to investigate how far aerogels can be synthesized with all the sol-gel varieties, and how far they advantageously can be used

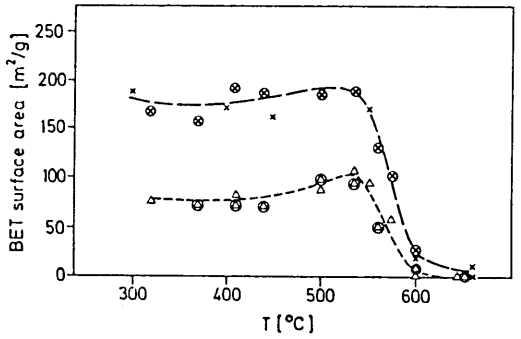


Fig.6a BET surface areas of two sodiumborosilicate gels; a: 7 % Na_2O; b: 14 % Na_2O (wt.-%) as a function of T [35]; encircled symbols: second independent measurement

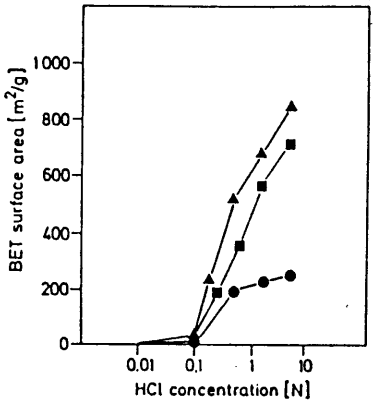


Fig.6b BET surface of dimethyl group containing gels as a function of CH_3-content and pH [36]; ▲ = 20; ■ = 40; ● = 60 (mole-% $(CH_3)_2SiO$)

as precursors for dense materials, or how far they can be used as derived. Of special interest may be the introduction of transition metals, e.g. in order to vary optical properties [39].

But not only inorganic modifiers but also organic network modifiers can be incorporated into an inorganic network by the sol-gel process. As mentioned above, the organic grouping can be introduced by use of an organosilicoesters of the type $R'_n Si(OR)_{(4-n)}$ where R' is an organofunctional group e.g. vinyl, amino, carboxy. Since a big number of different R' can be introduced, a big variety of the material synthesis is possible [39, 40]. The possibility of producing high surface area materials with organic groups was shown in fig.4. The aerogel process was not investigated with this type of material so far. A limitation may occur by insufficient stabilities of some organic groupings, but despite that limitation it seems to be an interesting possibility.

5. Conclusion

Since the sol-gel process in general leads to gel-like structures via a condensation process, more or less porous materials result. Since the main target of material synthesis was to produce dense products no big interest was shown in the possibilitiy of the production of extreme low-density materials. The primary structure is built up during the condensation process, that means the chemistry of this process has to be investigated very thoroughly, especially if multicomponent systems are synthesized. The sol-gel process offers a big variety of components (network formers and network modifiers, including organics, dopings) so that a wide material development potential exists. Further investigations have to show how far this potential can be used for the aerogel process.

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