

MECHANISMS AND KINETICS OF THE HYDROLYSIS AND CONDENSATION OF ALKOXIDES

H. SCHMIDT and H. SCHOLZE

Fraunhofer-Institut für Silicatforschung, Neunerplatz 2,
D-8700 Würzburg, F.R.G.

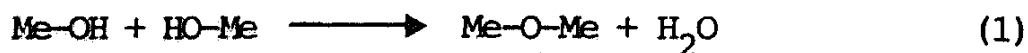
ABSTRACT

Hydrolysis and condensation of alkoxides involve different reaction steps. Generally the first step is the dissolution of monomers in organic solvents like alcohols. The second step is hydrolysis, where in most cases condensation may not be separated. Dissolution may incorporate solvation, coordination, complexation or polymerization. The addition of water leads to hydrolysis of Si-O-C bonds and subsequently condensation of silanols takes place. Another possibility of reaction is the hydrolysis-free condensation. As a function of reaction conditions and starting material different possibilities and mechanisms may take place. General conclusions are hardly to be drawn, since the comparison of data is difficult. In the paper theoretical models are reviewed and compared with experimental data. Conclusions with respect to the formation of solid materials are drawn.

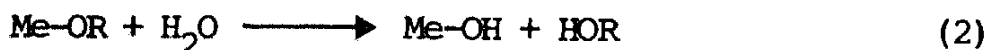
1 INTRODUCTION

The traditional way to prepare inorganic polymers is the use of solid compounds which generally are polymeric (crystalline or amorphous). In order to perform these reactions, high temperatures have to be applied, since thermal cleavage of the polymeric bonds is necessary in order to form new compounds. In the field of organic polymers in opposition to this, the general way is to use monomeric compounds and to apply one of the common crosslinking mechanisms (polycondensation, polyaddition, polymerization). The possibility to produce inorganic polymers by one of these mechanisms exists, too. Generally it is the polycondensation me-

chanism, since polymerization or polyaddition at least in the case of non-metallic inorganic materials based on the metal to oxide bond is not possible, if one excludes methods like chemical vapour deposition. A simple mean to form metal oxide bonds by a polycondensation mechanism is the condensation of metal hydroxides (eq.1):



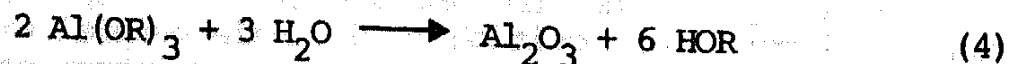
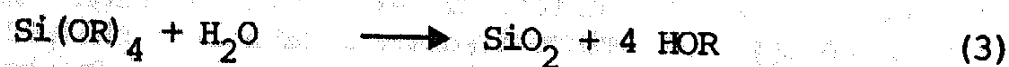
The preparation of metal hydroxides may be performed very simple for example by use of aqueous solutions of metal salts and changing of the pH to a value, where hydroxides may be precipitated. This reaction is well-known and often used for the preparation of synthetic powders for ceramics. The disadvantage of this reaction normally is that the reaction control is very difficult. Another reaction which allows a better control is the hydrolysis of alkoxides (eq.2):



The main advantage of this route is the possibility to run the reaction in a way that precipitation can be avoided and gels of high homogeneity can be formed. The possibilities to form materials for practical use first was systematically shown by the work of [1] and [2]. In the past many authors discovered the interesting possibilities of this route known as the sol-gel process [3-10]. The process leads (starting with monomers, in general alkoxides) through hydrolysis, condensation, densifying and mostly firing to dense materials. If one considers the hydrolysis and condensation reaction of alkoxides, it does not make any basic difference, if the chosen system leads to glasses, glass ceramics or ceramics. Moreover, the basic considerations are valuable, too, for alkoxides containing, non-hydrolyzing Si-C bond ligands, a possibility to introduce organic radicals into inorganic structures.

2 FUNDAMENTAL CONSIDERATIONS

The reaction path roughly described above indicates that very different reaction steps are included and that the total reaction is a very complex one. The simple reaction route (eqs. 3 and 4):



does not represent in any way this complexity. The pure thermodynamical standpoint leads to the conclusion that crystalline

SiO_2 and Al_2O_3 should be the final products. In reality in both cases at first amorphous gels are formed as a consequence of the crosslinking reaction of the reactive intermediates.

It is well known that, as a function of reaction conditions, the properties of these gels, especially with respect to their ability to be dried and densified, differ strongly [11-14]. The difference of these properties must be due to the different structures formed during the first step of polymer formation, that means, the first step of condensation. This fact leads to the question at which stage of the reaction stable structures may be formed or at which stage of the reaction parameters occur which influence the formation of these structures. Another question is to which extent these structures are able to survive the whole processing and determine properties of the formed materials.

A scheme which points out the main processing steps which not necessarily have to be carried out altogether, starting from hydrolysis and ending up with a molded material is given in table 1.

Table 1. Scheme of possible reaction steps of the material formation during the sol-gel process (The dots indicate to which extend the single reaction steps may expand.)

1. Hydrolysis (in solution) ...
 2.Condensation ...
 3. Drying.....
 4. Densification.....
 5. Sintering.....
 6. Crystallization...
 7. Molding
- material

Table 1 indicates that the different reactions are not necessarily chronological, but partly may take place at the same time, e.g. sintering and crystallization or condensation and molding (fiber drawing). In principle all these steps may include reactions with parameters influencing the material properties.

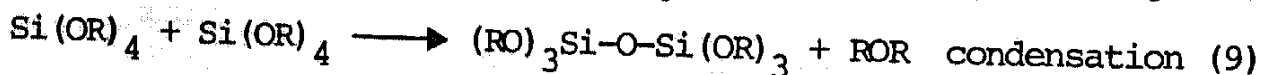
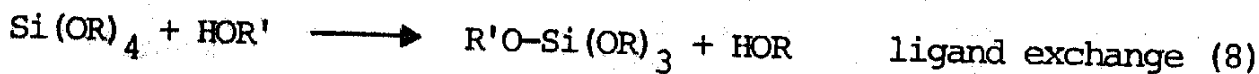
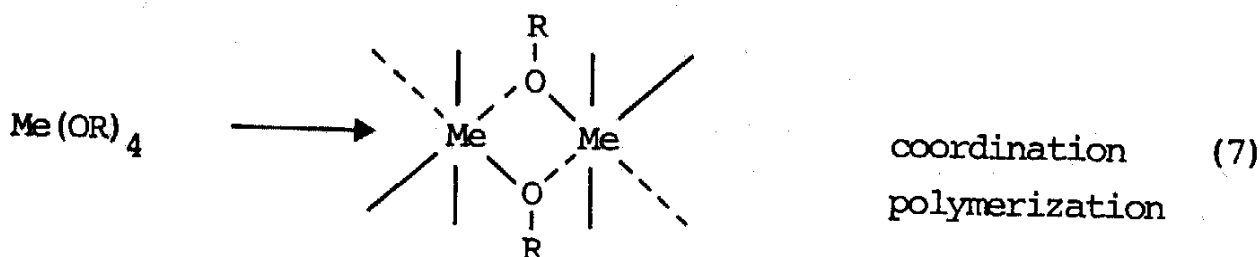
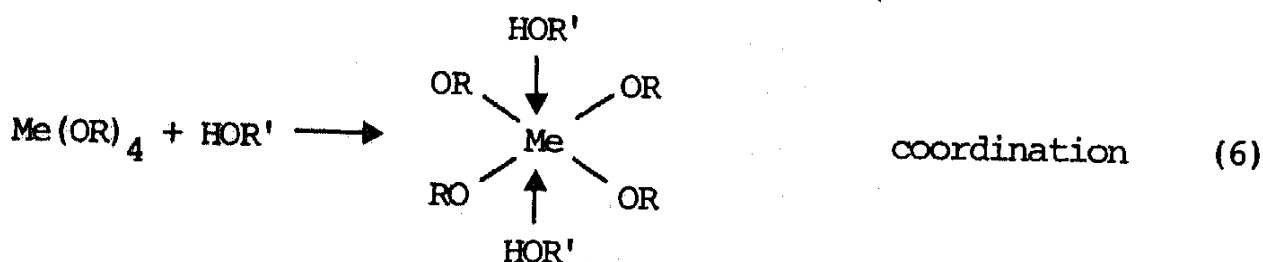
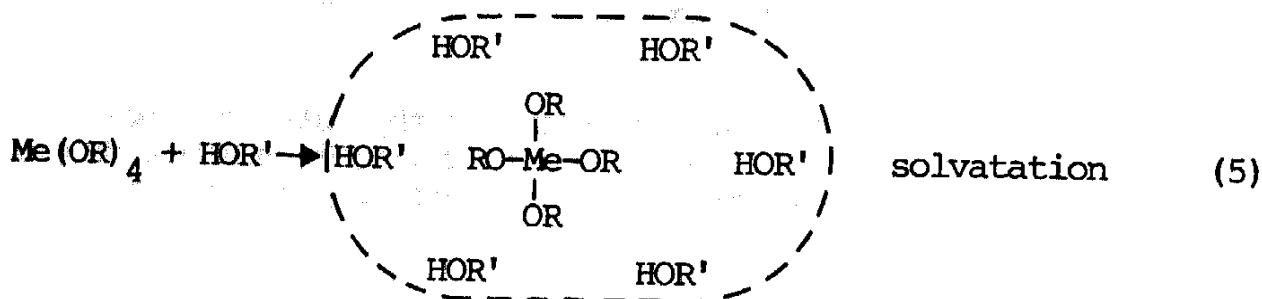
If one looks into the details these reaction steps become even more complex and the state of art with respect to the connection between reaction parameters and material properties shows a lack of data. One of the main reasons for this is the sensitivity of these reactions to reaction conditions, like solvents, catalysis, the role of water, and so on. This sensitivity makes

it very difficult to compare data of different authors. In this paper the attempt is made to point out the basic problems of reaction mechanisms and reaction kinetic in the two first main steps of the sol-gel process, hydrolysis and condensation.

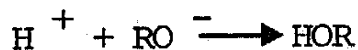
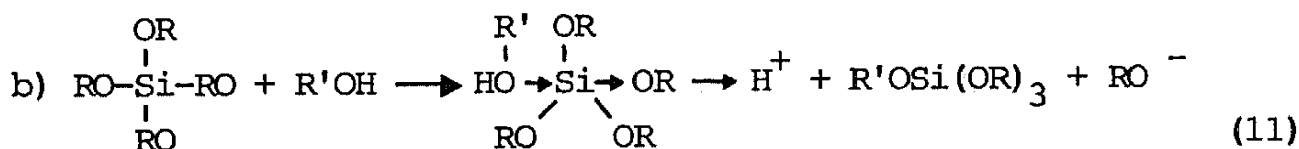
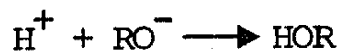
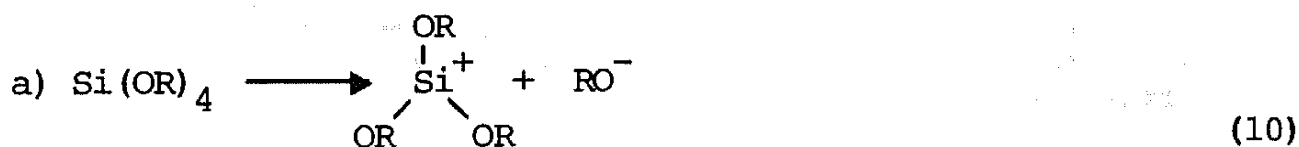
3 HYDROLYSIS AND CONDENSATION

3.1 Solutions of One-Component Systems

A one-component system, like $\text{Si}(\text{OR})_4$ or $\text{Al}(\text{OR})_3$, has the advantage that an interaction of two or more different components cannot take place. The first step generally performed to make materials by the sol-gel process from alkoxides, is to put the components into a solvent like alcohol. The question arises, if there are structure-forming reactions in solution. There are different possibilities: solvation, coordination, coordination polymerization, ligand-exchange, and polycondensation.



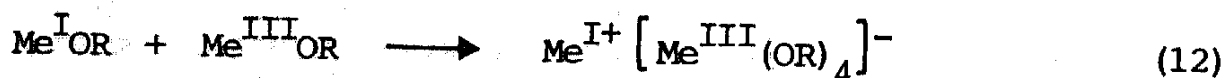
Equation (6) and (7) only may take place, if the coordination number is increased. This is unlikely with Si under these conditions, but well-known with Al. Higher coordination numbers are not required with equation (5), (8), and (9), at least not, if one considers the over-all reaction only. The question of the formation of complexes in solution is an important one, since the complex formation may influence the hydrolysis rate strongly, and, if coordination polymerization structures are formed, they may be partially kept up in the polymers formed by condensation. Coordination polymerization is unlikely with tetraalkoxysilanes. At least viscosity measurements done by our own with mixtures of tetraethoxysilane and ethanol show an additive behaviour. But with aluminum alkoxide as shown by Bradley [15], a strong tendency of coordination polymerization is observed. These reactions strongly should be influenced by the type of central atom (e.g. Si, Al, Ti, B), the ligand (length of the chain "R"), and the solvent. Unfortunately there are not much structural details known about these reactions. This is understandable, since the evaluation of structures of liquids is rather difficult. Equation (5) (solvation) should take place with most solvents, if alkoxides are dissolved. The reaction number (8) (ligand exchange) is described by different authors [16-18]. But almost no kinetic data are known. The reaction is important, since the rate of hydrolysis depends strongly on the type of ligand, that means, if an alkoxide is dissolved in an alcohol, where the alcoholic OR is not identical with alkoxide OR, ligand exchange will take place and the hydrolysis rate will change with time. The mechanisms of this reaction may be described by equations (10) and (11).



Reaction (10) requires a trivalent transition state, reaction (11) requires a pentavalent one. Different authors [19-21] postulate a pentavalent transition state, but there is no experimental proof for orthoesters. The stability of a trivalent siliconium ion depends very strongly on the type of ligand, e.g. the +I-effect of these ligands. The pentavalent state should lead to a change of conformation. This type of reaction was investigated by Sommer et al. [21], but with optically active organoalkoxysilanes. But is not quite clear, as far as the reaction of organoalkoxysilanes may be transferred to alkoxysilanes. The reaction (9) does not take place at room temperature [22], but at higher temperatures it may add remarkably to the condensation.

3.2 Solution of Multicomponent Systems

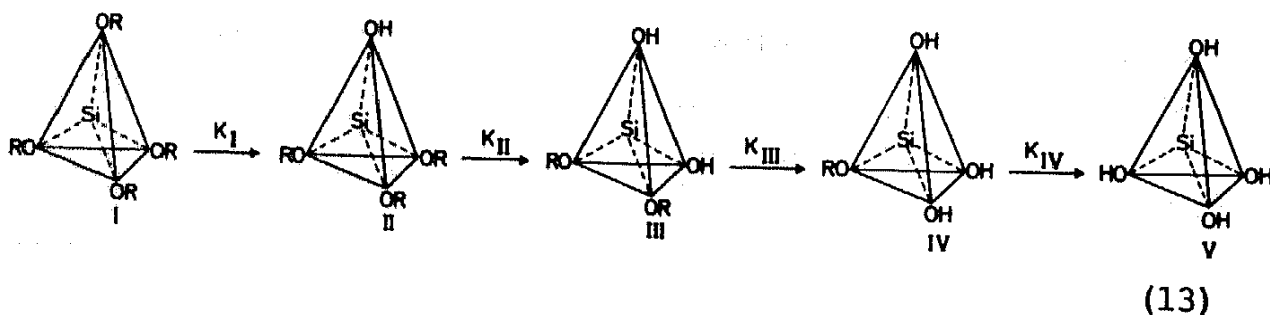
In this case interaction between different types of alkoxides has to be considered. Especially as a function of difference in lewis acidity, complexation of two different components may occur as it takes place, if one adds a Me(I) alkoxide to a Me(III) alkoxide as indicated in equation (12).



This very easily takes place e.g. with sodium alkoxide and aluminum or boron alkoxide. The reactivity, in case of hydrolysis of these complexes, should be different to that of single components so that a non-additive behaviour should occur. There are rather good imaginations of structures of different (especially transition metals) alkoxides in solutions developed by Bradley [15]. But there are almost no data on interactions of mixtures of glass and ceramics forming alkoxides and the influence on processing and properties of these interactions.

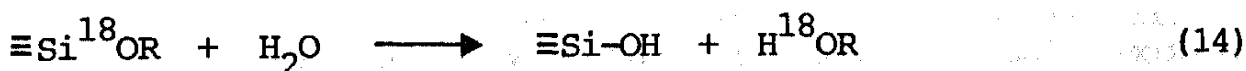
3.3 Reaction with Water

The most common step for the performance of the sol-gel process is to add water to the solution of alkoxides. In the case of a Me(I) alkoxide like sodium alkoxide, hydrolysis reaction is a very simple one. In the case of multifunctional elements like silicon a 4-step reaction has to take place for total hydrolysis as it is shown in equation (13).

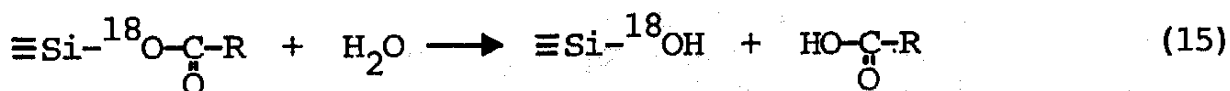


In this reaction mixture five different types of monomers are possible as they are indicated with the numbers I-V. For each reaction step different rate constants (K_I to K_{IV}) are possible. Since there is no necessity for identical reaction rates, and if these reaction rates are different there must be a population profile which is changing the time and which defines the number of reactive monomers. If the condensation rate is proportional to the number of reactive polymers, the formation of different structures occurs with time.

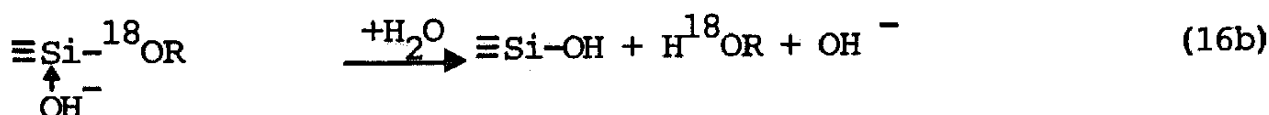
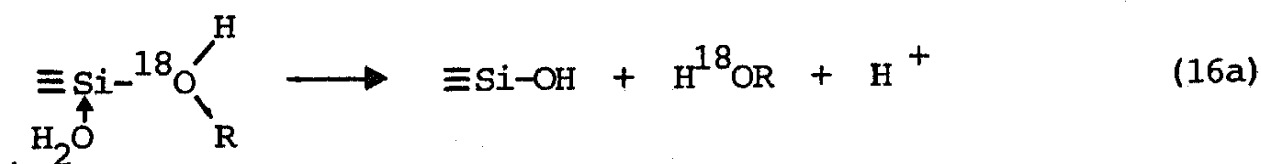
In order to get an imagination on mechanisms and since no data are available, one has to consider closer the basic steps of these reactions. The first question which arises is, what can happen, if the OR is changed to OH. The first, who investigated this question in detail, was Khaskin [23]. He used ^{18}O in order to find out, if a dissociative or a non-dissociative substitution of an OR group by an OH group takes place. His results show that with alkoxysilanes a dissociative reaction occurs.



This dissociative reaction takes place with acid and basic catalysis and with organosilanes. But in the case of acyl ligands the reaction mechanism is a non-dissociative one.



From these facts one can follow that in the case of alkoxides, where an OH group exchanged by an OR group, a nucleophilic attack of OH^- ion (basic catalysis) or an H_2O molecule (acid catalysis) takes place. In the case of alkoxides this attack aims to the silicon atom, since the silicon atom carries the highest positive charge (eqs. 16a and b).



In the case of the acyl compound the nucleophilic attack aims to the carbonyl carbon atom as the carrier of the highest positive charge.

As indicated in equation (16a) in the case of proton catalyzed reactions, an oxonium complex will be formed by the protonation of the oxygen atom of the OR group. This increases the positive charge of the Si-O bond of the silicon atom and enables the H₂O molecule despite of its low nucleophilic power to attack the silicon atom. The dissociation of this transition complex leads to the cleavage of the Si-O bond, while a new Si-O bond from the H₂O molecule will be formed. In the case of the basic catalysis the OH⁻ ion is able to attack the silicon atom directly as a consequence of its higher nucleophilic power. These mechanisms can be deducted from the results of Khaskin, but this does not allow to say anything about the conformation of the transition state. But it is possible to deduct prognoses with respect to parameters which may influence the reaction kinetics. That means that all facts which increase concentration of transition complexes from equation (16a) or (16b) should increase the reaction rate. These parameters should be the concentration of H₂O, if there are no superposing effects, the concentration of catalyst and parameters who increase the positive charge of the silicon atom. Since the concentrations of water and the catalyst might be chosen, the electronic state of the silicon atom is dependent on the type of the ligands. It is well known that the length of an alkyl chain determines the +I (electron pumping) effect. Longer chains show stronger +I effects. That means that the reaction rate should decrease as a function of the chain length, if the other parameters are kept constant. Measurements of Aelion et al., Akerman, Schmidt et al. [24-26] show that the hydrolysis and condensation rate decrease with increasing chain length. Another explanation for this might be the steric hindrance of longer chains, which makes it more difficult for a water molecule to attack the silicon atom. The results of Aelion and Akerman are given in table 2 and 3.

Table 2. Dependence of hydrolysis rate on the chain length of R (=SiOR)

R	$k \cdot 10^2, \text{ liters} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \cdot \text{H}^+^{-1}$
C ₂ H ₅	5.1
C ₄ H ₉	1.9
C ₆ H ₁₃	0.83
$\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{CH}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{CH}_2 \\ \diagup \\ \text{CH}_3 \end{array}$	0.30

Table 3. Dependence of gelling time on the chain length of R ($\equiv\text{SiOR}$)

Formula	Hydrolysis time up to gel formation, hr
$(\text{C}_2\text{H}_5\text{O})_4\text{Si}$	2
$(n\text{-C}_4\text{H}_9\text{O})_4\text{Si}$	32
$(\text{CH}_3(\text{CH}_2)_6\text{O})_4\text{Si}$	25
$(\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_4\text{Si}$	75
$(n\text{-C}_4\text{H}_9\text{O})(t\text{-C}_4\text{H}_9\text{O})_3\text{Si}$	236
$(\text{sec-C}_4\text{H}_9\text{O})_4\text{Si}$	500

Figure 1 shows the hydrolysis rate of tetraethoxysilane and tetramethoxysilane with different proton and water concentrations. The surprising effect of this experiment is that the hydrolysis rate decreases with increasing amounts of water. This might be due to the special experimental conditions and the water acting as a proton acceptor which decreases the proton activity.

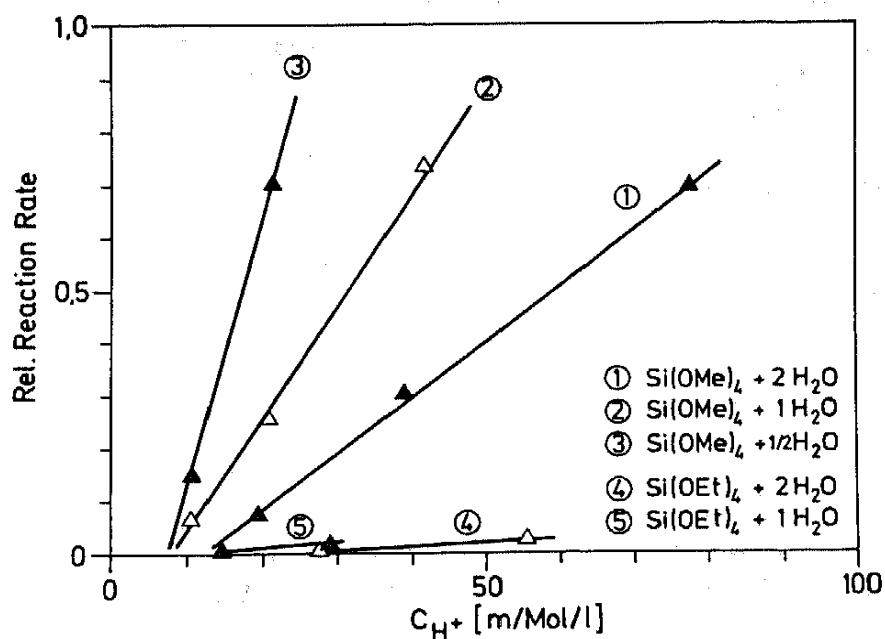


Fig.1 Dependence of hydrolysis rate on type of silane, H_2O and proton concentration; solvent: ethanol; volume ratio solvent: silane = 1:1; $T = 25^\circ\text{C}$; catalyst: HCl

Extensive investigations on the hydrolysis rates of different silanes the first time were carried out by Aelion and coworkers. They found a second-order reaction for the hydrolysis of tetraalkoxysilanes in dioxane as solvent, if excess of water is used (eq.17).

$$\frac{dx}{dt} = k \cdot c_{\text{H}_2\text{O}} \cdot c_{\text{silane}} \quad x = \text{number of reacting silane molecules} \quad (17)$$

In the basic catalyzed case a first-order reaction was observed (eq.18).

$$\frac{dx}{dt} = k \cdot c_{\text{silane}} + C \quad (C = \text{constant}) \quad (18)$$

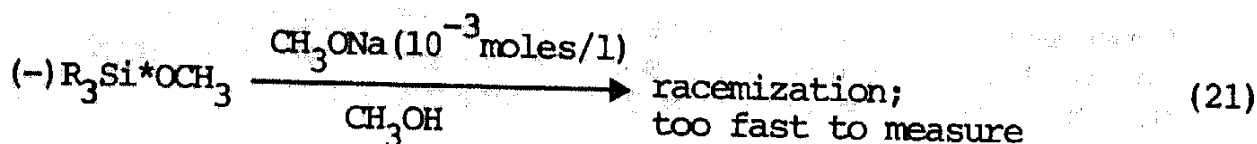
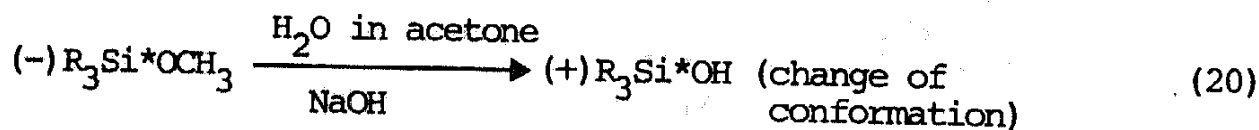
These rate laws cannot be generalized, since they are collected under very special experimental conditions and the general validity is not proved yet.

The rate dependence of k follows equation (19).

$$k = 0.051 \cdot c_{\text{H}^+} \quad (19)$$

Aelion also points out that the extent of hydrolysis depends on the H^+ concentration, that means that there is a pH dependent equilibrium which indicates that the role of the proton is not only a catalytic one. Measurements of Schmidt et al. [26,27] do not support these data, since there the hydrolysis equilibrium was found to be independent of the proton concentration. But these results are obtained with understoichiometric amounts of water and in ethanol as solvent. So these results are not quite comparable. Aelion postulates a pentavalent transition state without giving experimental proof for this.

The question, if a pentavalent or trivalent transition state is possible, is very difficult to be answered, since direct experimental data are lacking. From the work of Sommer [21] with trialkylalkoxysilanes with optical activity it is shown that hydrolysis in the most cases does not lead to racemization, but in some cases it does (eqs.20,21).



That means, in the second case the racemization is only explainable, if a trivalent transition state will be formed. But the question cannot be answered, if these results obtained from alkylalkoxysilanes are valid for tetraalkoxysilanes.

The influence of an alkyl ligand on the silicon atom should be of a +I type. But since in the case of the oxygen silicon bond a partially π -bond is possible, in the case of a Si-C bond it is not since carbon does not have any π -orbitals. So it is very difficult to estimate the differences between the electronic effects of OR or R bonds on the silicon atom.

Since there is an experimental proof that with increasing chain length of the OR groups the hydrolysis rates slows down, one can think about the influence of the substitution of an OR by an OH group in the tetraalkoxides of silicon. The OH group exhibits a lower +I effect as an OCH_3 or OC_2O_5 group. So a partially hydrolyzed silicon tetraalkoxide should have a higher positive charge on the silicon atom and should show an increased hydrolysis rate, compared with the silane containing one OR group more. On the other hand, the probability of the hydrolyzation of an OR group in a silicon group is proportional with the number of OR groups. So that even if the rate constants are the same, one OR group of the tetraalkoxysilane would be hydrolyzed as much as one OR group of a silane containing two OR groups. The question is which distribution of monomers, as a function of reaction condition and time, will occur and, if this distribution may be influenced in order to receive useful properties. The hydrolysis reaction of tetraalkoxysilane which leads to monomers with only two hydrolyzed OR groups are able to form linear polymers (in analogy to dimethyldiethoxysilane). This type of polymers should be very useful for fiber drawing, and investigations of Sakka [9] show that under certain reaction conditions, especially with acid catalysis and understoichiometric amount of water, spinable polymers are formed, indicating a certain linearity. Rheological measurements support this hypothesis. From Brinker et al. recently [28] experimental data were given, pointing out that hydrolysis and condensation rates depend very strongly on pH over a wide field, and in addition to that two types of structures could be evaluated as a function of pH (Fig.3 and 4). These experiments were carried out with tetraethoxysilane. From Schmidt et al. similar results were obtained (Fig.5) with alkylalkoxysilanes and alkoxysilanes [29]. Brinker points out that in the acid case a more linear chain growth takes place than in the ammonia catalyzed, indicating that in the acid case monomers with two condensable (OH) groups are formed preferably. But up to now no mechanistical hypothesis exists in order to explain these facts in a satisfying way. This theory of Brinker may be supported by work of Bechtold et al. [30], who concludes from light scattering

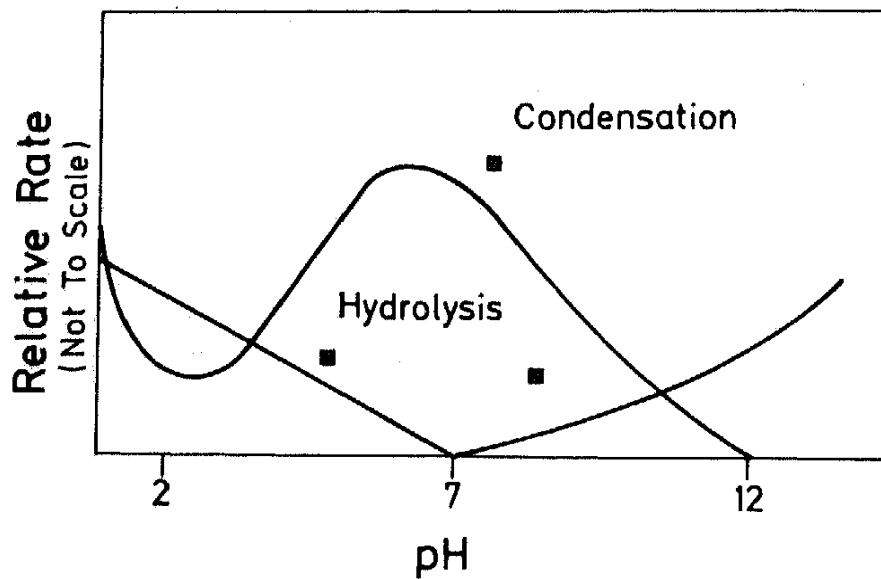


Fig.3 Rate dependence of hydrolysis and condensation of tetra-alkoxysilane on pH

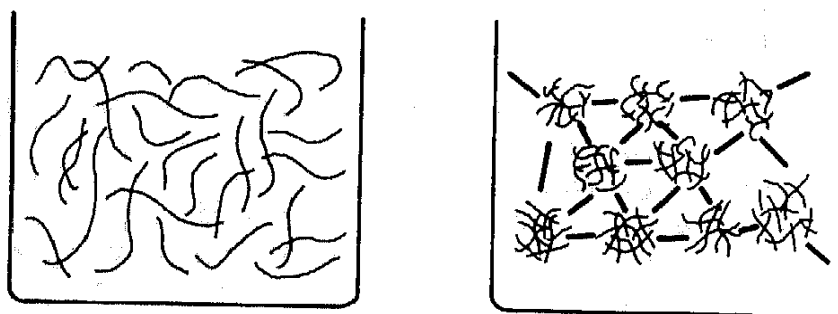


Fig.4 Structure evaluation of gels from (a) acid and (b) basic catalysis of hydrolysis and condensation of tetraalkoxy-silane

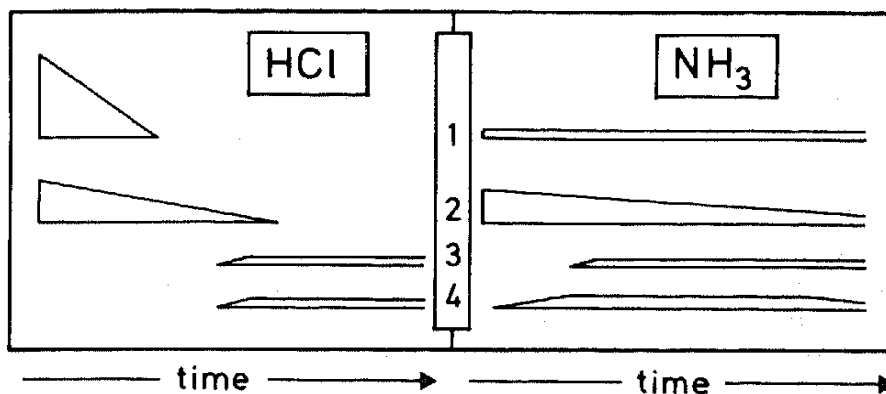
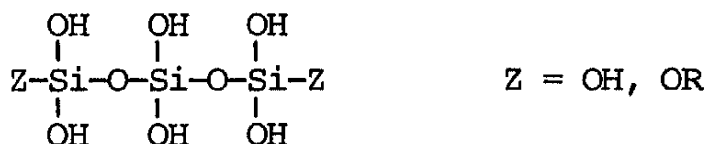


Fig.5 Scheme of chronological order of the single reaction steps of gel formation with HCl and NH_3 catalysis. The ordinate expansion of the bars refers to the reaction rate.
 Hydrolysis of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ (1) and $\text{Si}(\text{OC}_2\text{H}_5)_4$ (2)
 Condensation of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ (3) and $\text{Si}(\text{OC}_2\text{H}_5)_4$ (4)

experiments and statistical calculations that units of the type



exist.

One possibility to follow the hydrolysis reaction of alkoxy-silanes in one-component systems would be to monitor the methylene protons by NMR spectroscopy. Hopeful attempts were made by Assink et al. [31], who are able to distinguish between the methylene protons of an alkoxy-silane and of alcohols. Up to now the resolution of the NMR experiments is not high enough to distinguish quantitatively between the different hydrolyzed steps.

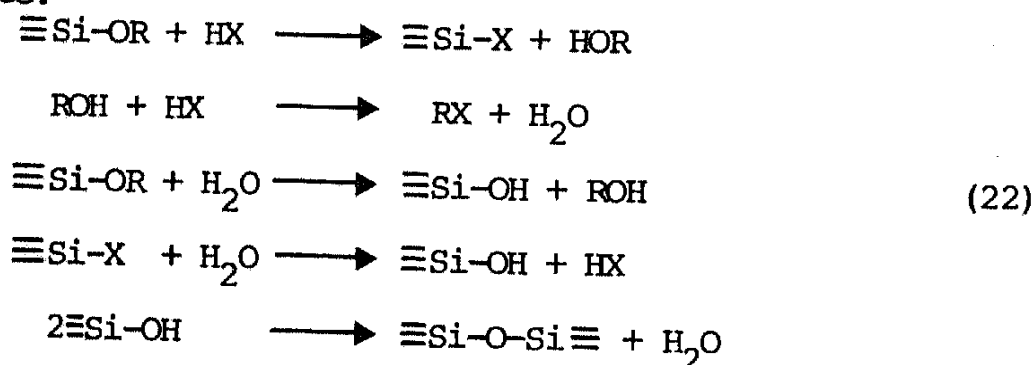
A behaviour similar to tetraalkoxysilane is reported from tetraalkoxytitanium [6,15,32]. The hydrolysis rates of titanium alkoxide are far higher than those of the analogous silicon compounds. Unfortunately only few data on the hydrolysis and condensation rates of other alkoxy compounds are available. The knowledge of the relative rates of the different components is very important in multicomponent systems, since the concentration of the polymerizable monomers is a function of the hydrolysis rate of their starting compounds. By this, the structure of a polymer can be influenced very strongly. If one compares e.g. the system of tetraethylsilicate and tetraethyltitanate in ethanol and one adds water, titanium oxide will precipitate and the ethyl silicate will hydrolyze only very slowly. By variation of reaction conditions it is possible to avoid precipitation of titanium and to get homogeneous looking gels, but there is no proof, how homogeneous they really are. There might be structure elements which mainly consist of titanium oxide chains, as a consequence of the higher hydrolysis and condensation rate of Ti-alkoxides compared to the Si.

Experiments of Schmidt and Scholze [27] showed that in a borosilicate system sodium alkoxide and boron alkoxide show the far quickest hydrolysis rate. If the three-component system is hydrolyzed, non-additive behaviour occurs indicating some interaction between the single components, where a type of complexation (formation of a sodium borate complex) is probable. This shows again that structures may be formed in a very early stage.

3.4 Reaction without Water

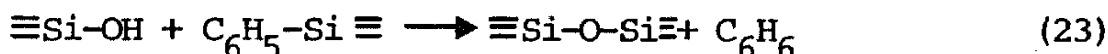
As indicated in equation (9) in principle it is possible that alkoxysilanes react to a polymer network without the addition of water. Two basic types of reaction may be distinguished: There is the direct reaction of two Si-OR groups which under special conditions may form a Si-O-Si group under the formation of ether. This reaction takes place at temperatures of about 200°C and is described by Noll.

Another type of reaction is described by Voronkov et al [16] where the solvent is involved (eq.22). In this reaction, no water is added to the reaction mixture, but water is formed as an intermediate:



The condensation reaction then is the reaction of the Si-OH group with one Si-OR group under the formation of alcohol. Schwarz et al. [33] described a reaction where by the use of alkoxides with longer chains Si-O groups under the formation of olefines are described. These Si-O groups then lead to condensation with other OR groups. Mazdidasni et al. [3] used this reaction for the formation of reactive powders from different alkoxides. This reaction takes place at temperatures around 200°C and may be used for the formation of polymers based on the metal oxide bond starting from alkoxides and without using water.

Another possibility to form a inorganic polymer structure is the silanolysis reaction as described by Schott et al. [34]. They found out that especially phenylalkoxysilanes may be used for this reaction where the Si-O group attacks the silicon carbon bond which is cleaved by the formation of an silicon oxygen bond.



This reaction in special cases may be used, too, for the formation of polymers.

Reaction conditions without the use of water can be successfully applied in all cases, where the additon of water leads to complications, like precipitations, inhomogenities based on extremely differnt reaction rates or the demand of low water contents in gels.

4 CONCLUSIONS

If one starts to think about the formation of the materials by the sol-gel process and wants to use alkoxysilanes as starting materials, a couple of mechanistical questions arises. The first is the correlation of reaction rates and material properties. Therefore detailed data of the reaction rates, hydrolysis and condensation rates of different alkoxysilanes should be available. Unfortunately only a few data on alkoxysilanes are known and since they depend on very special reaction conditions, they are not able to be generalized. So the present state is that each researcher has to work out his own set of reaction data.

In order to be able to use the nice tool of a sol-gel processing for the material preparation better than it is possible in the moment, these data should be evaluated as soon as possible. Table 4 gives a survey on the present state over this field.

Table 4. Reaction Parameters Influencing Hydrolysis and Condensation

Parameter	Effect	Data available	Consequences
Type of Metal	Rate Structure	Only on Si alkoxides	Kinetics should be determined, especially on other alkoxides
Hydrolyzable Ligand	Rate	Detailed investigations often on organoalkoxy-silanes	Reaction rates can be influenced
Solvent	Equilibrium Rate	--	Determines number of unhydrolyzed residues, structure of gels
Water	Equilibrium	Only on Si alkoxides	Degree of hydrolyzation structure of glass, data on others required
Catalyst	Rate Branching Structure of gels	Only on Si alkoxides (kinetics) Structure models evaluated as a function of H ⁺ and OH ⁻	Data on others required
Temperature	Rate Structure?	--	Data to be evaluated
Vapor Pressure (H ₂ O)	Rate (at low pressures), Structure (at high pressures)	On Si alkoxides and on aerogels	More data could provide good means for tailoring

5 REFERENCES

- 1 Roy R., J.Amer.Ceram.Soc. 52 (1969) 344.
- 2 Dislich H., Angew.Chem. 83 (1971) 428.
- 3 Mazdiasni, K.S., R.T.Dolloff and J.S.Smith, II. J.Amer.Ceram.Soc. 52 (1969) 523.
- 4 Mukherjee, S.P. and J.Zarzycki. J.Mater.Sci. 11 (1976) 341.
- 5 Yoldas, B.E. J.Mater.Sci. 12 (1977) 1203.
- 6 Kamiya, K. and S.Sakka. Res.Rep.Fac.Eng.Mie Univ. 2 (1977) 87.
- 7 M.Nogami and Y.Moriya. J.Non-Cryst.Solids 37 (1980) 191.
- 8 Carturan, G., V.Gottardi and M.Graziani. J.Non-Cryst.Solids 29 (1978) 41.
- 9 Sakka, S. and K.Kamiya. J.Non-Cryst.Solids 43 (1980) 403.
- 10 Mackenzie, J.D. J.Non-Cryst.Solids 48 (1981) 1.
- 11 Yoldas, B.E. J.Non-Cryst.Solids 51 (1982) 105.
- 12 Brinker, C.J., K.D.Keefer, D.W.Schaefer and C.S.Ashley. J.Non-Cryst.Solids 48 (1982) 47.
- 13 Partlow, D.P. and B.E.Yoldas. J.Non-Cryst.Solids 46 (1981) 153.
- 14 Zarzycki, J. J.Non-Cryst.Solids 48 (1982) 105.
- 15 Bradley, D.C. et al. Inorganic Polymers. (Academic Press, New York 1962)
- 16 Voronkov, M.G., V.P.Mileshkevich and Y.A.Yuzhelevskii. The Siloxane Bond (Plenum, New York, London 1978).
- 17 Andrianov, K.A. Organic silicon compounds (State Sci.Publ.House for Chemical Literature, Moscow, 1955)
- 18 Sheefer, D.W. Proc.Mater.Res.Soc.Spring Meeting 1984, Albuquerque, USA
- 19 Swain, C.G., R.M.Esteve Jr and R.H.Jones. J.Amer.Chem.Soc. 71 (1949) 965.

- 20 Keefer, M.D. Proc. Mater. Res. Soc. Spring Meeting 1984, Albuquerque, USA
- 21 Sommer, L.H. and C.F. Frye. J. Amer. Chem. Soc. 82 (1960) 3796.
- 22 Noll, W. Chemie und Technologie der Silicone. 2. Auflage (Verlag Chemie, Weinheim, 1968).
- 23 Khaskin, I.G. Dokl. Akad. Nauk SSSR 85 (1952) 129.
- 24 Aelion, R., A. Loebel and F. Eirich. J. Amer. Chem. Soc. 72 (1950) 5705.
- 25 Akerman, E. Acta Chem. Scand. 10 (1956) 298; 11 (1957) 298.
- 26 Schmidt, H. and A. Kaiser. Glastechn. Ber. 54 (1981) 338.
- 27 Schmidt, H., H. Scholze and A. Kaiser. J. Non-Cryst. Solids 48 (1982) 65.
- 28 Brinker, C.J. et al. Proc. Mater. Res. Soc. Spring Meeting 1984, Albuquerque, USA.
- 29 Schmidt, H., A. Kaiser and H. Scholze. J. Physique 43 (1982) 275.
- 30 Bechtold, M.F., R.D. Vest and L.P. Plambeck Jr. J. Amer. Chem. Soc. 90 (1968) 4590.
- 31 Assink, R.A. Proc. Mater. Res. Soc. Spring Meeting 1984, Albuquerque, USA.
- 32 Kamiya, K. et al. J. Mater. Sci. 15 (1980) 1765.
- 33 Schwarz, R. and K.G. Knauff. Z. anorg. allg. Chem. 275 (1954) 176.
- 34 Schott, G. and H. Berge. Z. anorg. allg. Chem. 297 (1958) 32.