

*Part I. Basic investigations on hydrolysis, condensation and densification I*

**PRINCIPLES OF HYDROLYSIS AND CONDENSATION REACTION  
OF ALKOXYSILANES**

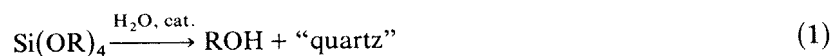
H. SCHMIDT, H. SCHOLZE and A. KAISER

*Fraunhofer-Institut für Silicatforschung, Würzburg, Fed. Rep. Germany*

Alkoxysilanes are used as starting materials for network formers in the sol-gel process. Substitution of an Si-O-bond by an Si-C-bond allows the introduction of organic radicals into a siliceous network. Since the hydrolysis and condensation reactions strongly effect the properties of the developed materials, it is necessary, in order to prepare specific materials, to understand the basic mechanisms of these reactions. Hydrolysis and condensation of alkoxysilanes have a long history and basic investigations with regard to mechanisms are carried out from very different points of view. Papers from different fields are reviewed and basic results of the co-condensation of  $\equiv$  Si-C-containing with non  $\equiv$  Si-C-containing silanes are reported.

**1. Introduction**

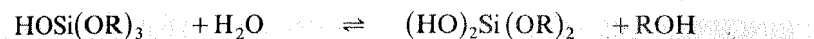
Alkoxysilanes play an important role in the development of silicon-containing materials. Tetra-alkoxysilanes are useful compounds for preparing glasses and glass ceramics by the sol-gel process. Substituted (e.g. alkyl- or aryl-)alkoxysilanes are used as starting compounds or appear as intermediates in the manufacturing of silicones, and in combination with tetra-alkoxysilanes or other network formers they serve as precursors for the preparation of heteropolysiloxanes. The hydrolysis of tetra-alkoxysilanes leads to alcohol and SiO<sub>2</sub> and from thermodynamical reasons, quartz should be formed, since quartz at room temperature is the stablest modification:

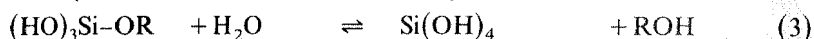


Under average reaction conditions, e.g. in an alcoholic solution, or with water only (two-phase-reaction as a result of the immiscibility between the alkoxysilane and water), the reaction leads to different types of intermediates, starting with oligomeric silicic acids or oligomeric esters and ending up in gels or powders with considerable contents of water and inhomogeneous microstructures. Even heating up in most cases at first leads to glassy and non-crystalline products.

Considering the over-all reaction [eq. (1)] one can see that, since alcohol is involved as a reacting component, the concentration of alcohol is able to be

involved in the hydrolysis equilibrium, according to eqs. (2) to (4). Eqs. (4) and (5) affect condensation.



$$\vdots$$


This demonstrates that the reaction from an alkoxy silane to a solid material is not a simple one, but many different intermediates are possible. That means that it is very hard to give an exact thermodynamical description of what might be possible or not in these complicated reaction paths. As a consequence, it is not possible to give detailed thermodynamically based prognoses, and the effect of the different reaction parameters (organic radical of the OR group, solvent, catalyst, temperature, concentration) has to be investigated experimentally, and the conclusions have to be drawn from these results.

In the literature numerous publications concerning the processes of hydrolysis and condensation of alkoxy silanes exist for different reasons. Moreover, in the last 15 years this subject was investigated by authors working on the sol-gel process for preparing glass, glass ceramics and ceramics [1-10]. This is understandable, since the hydrolysis and condensation of alkoxy silanes as potential network formers play an important role in this process as mentioned above.

It is not possible to give a survey of the state of the art concerning the reaction of alkoxy silanes in this paper, but the results of some authors will be reviewed, which in general are not discussed in sol-gel literature, since they are not directly related to this field, but deal with the reaction of alkoxy silanes for other reasons.

## 2. Reaction of silicoorthoesters

### 2.1. Hydrolysis and condensation

If silicoorthoesters are hydrolyzed, especially if one wants to prepare solid materials, it is very difficult to separate hydrolysis from condensation. That means that in most cases reactions according to eqs. (4) and (5) will start very soon after eq. (2), and, if the degree of polymerization has reached a sufficient state, gelation occurs. For this reason, most papers deal with both, hydrolysis and condensation. During the last decade the sol-gel transition and especially the densification and the formation process of monolithic  $\text{SiO}_2$  glass have been investigated by different authors. One of the interesting subjects of these papers is the question, how does condensation influence gelation or, more

general, which parameters lead to precipitation on the one hand and gelation on the other? Since it is not possible to determine quantitatively the crosslinking mechanism, a lot of models have been developed by indirect conclusion. In Iler's book [11] these theories are reviewed. Partlow and Yoldas [12] pointed out that the condensation reaction determines the primary structure of the prepared gels and their properties. They found that  $\text{SiO}_2$  gels prepared by different methods show different abilities of forming monolithic glasses.

The reactions of silicoorthoesters have been of interest for a long time. In the beginning investigations were carried out to determine their physical and chemical properties, and in this connection it was found that silica gel was formed by the reaction of  $\text{Si}(\text{OR})_4$  with water.

The first to investigate the reaction of an oxygen-containing organic silicon compound, in this case tetraethoxysilane, was Ebelmen [13] in 1844. He observed the hydrolysis and condensation of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  and found, as a function of the addition of water, well defined oligomers like hexaethoxydisiloxane and octaethoxytrisiloxane. Total hydrolysis and following condensation of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  and  $\text{Si}(\text{OC}_5\text{H}_{11-i})_4$  led to silica gel and, as described by Ebelman, after some months storage at room temperature to clear monolithic products with the shine of crystalline quartz, a specific weight of  $1.77 \text{ g/cm}^3$  and a hardness able to scratch glass. That means that basic principles of the sol-gel process were discovered about 140 years ago. Between 1860 and 1870 similar results were obtained by Friedel, Ladenburg and Crafts [14–16].

The work of Ebelman and Friedel et al. had experimentally proved that no simple reaction according to eq. (1) takes place. Since under mild conditions (e.g. refluxing) hydrolysis is an indispensable step and this step requires water as a reactant, it should be possible to isolate intermediates by the simple means of restricting the amount of water to the reaction mixture. Thus, theoretically only a part of the  $\equiv\text{Si}-\text{OR}$  groups is able to react to  $\equiv\text{Si}-\text{OH}$  groups and to condense to siloxane bonds ( $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ ).

The first to investigate systematically the role of water in its reaction with alkoxysilanes were Konrad et al. in 1929 [17]. They carried out the hydrolysis of  $\text{Si}(\text{OCH}_3)_4$  with an addition of understoichiometric water in varying amounts. Analysis of the reaction products led to the conclusion that hydrolysis is accompanied by condensation and that the role of the water must be a reacting one. They found that the degree of polymerization follows eq. (6):

$$p = \frac{n}{n - m} \quad (6)$$

where  $p$  = number of Si-atoms in the polymer,  $n$  = moles of  $\text{Si}(\text{OCH}_3)_4$ , and  $m$  = moles of water.

Thus, every desired degree of polymerization may be chosen by adding the calculated amount of water. Konrad et al. carried out their reactions with pure  $\text{Si}(\text{OCH}_3)_4$  and understoichiometric amounts of water, under these conditions water was reacted completely. The determination of the degree of polymerization does not provide any structural information about the oligomeric inter-

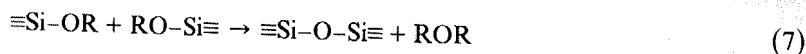
mediates. In the case of understoichiometric water addition one can conclude from the presence of unhydrolyzed groups, that more linear types of oligomers are present than in the case of excess water with total hydrolysis of  $\text{Si}(\text{OR})_4$  and the subsequent preference of a three-dimensional crosslinking.

Bechtold et al. [18] developed a hypothesis about this matter in 1968 and confirmed by experimental results that under reflux conditions hydrolysis of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  first leads to polymers of a type  $\text{Z}[\text{Si}(\text{OH})_2\text{OSi}(\text{OH})_2\text{OSi}(\text{OH})_2]_n\text{Z}$  with Z as a non-reactive end group, introduced in order to stop polymerization. Sakka and Kamiya [19] showed that partial hydrolysis of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  leads to linear polymers, too, but to polymers of the type  $[\text{Si}(\text{OR})_2\text{O}]_n$  with higher  $n$ . This type of linear oligomers may be important for special molding processes, e.g. fiber drawing.

Yoldas [20] recently published a theory, where he connected the hydroxyl content of a gel with the amount of water added to a reaction mixture of  $\text{Si}(\text{OC}_2\text{H}_5)_4$  and ethanol. In conclusion he proposed different structural models with different degrees of network connectivity without giving mechanistic explanations. Contrary to other authors [17–19] he proposes a spherical network expanding system during the particle growth process. Indeed, microstructures of silica gels very often display spherical particles, but there is no proof that spherical particles are affected by a three-dimensional crosslinking reaction [11,19,21–24]. Theoretical considerations about condensation, particle growth, and different mechanisms are given by Iler [11], Weyl [25], and Okkerse [26].

There should be a connection between condensation mechanisms and particle growth but the influence of the numerous reaction parameters has to be taken into consideration. Due to this fact no generally valid mechanisms including both condensation and particle growth, have been established as yet.

For practical use hydrolysis and condensation in a sol-gel process is usually carried out in alcoholic solution. In general, this causes an incomplete hydrolysis and leads to an equilibrium with a remarkable amount of unhydrolyzed  $\equiv\text{Si}-\text{OR}$  groups [27,28]. Since in the absence of water the thermal stability of the  $\equiv\text{Si}-\text{OR}$  group is rather good, in a sintering procedure these groups will disturb the densifying process. From different investigations it has been established that in principle a condensation at higher temperatures may take place by elimination of ether [29,30]:



A detailed study on this subject was carried out by Schwarz et al. [31,32]. They prepared polymeric esters by partial hydrolysis and condensation of  $\text{Si}(\text{OR})_4$  and proposed different types of condensation mechanisms at elevated temperatures. So they could prove two different mechanisms at about 200°C in the condensation of isopropyltetrasiloxane to the octaester. They analyzed di-isopropylether and propene as reaction products, but no water. This indicates that silanols are formed as intermediates, but do not react with each other. This type of reaction mechanism is important for the sol-gel transition

at elevated temperatures, if alcohol is used as a solvent, since in this case unhydrolyzed OR groups are present.

The cited results show that hydrolysis and condensation in alcoholic solution under well defined addition of water lead to oligomeric intermediates containing both OR and OH groups. In the case of an excess of water complete hydrolysis is possible and OR-free species, that means silicic acids as intermediates should be present, at least if diluted solutions are applied. These acids are instable and condensation will take place to form oligomers or polymers, e.g. gels. Monitoring the condensation reaction of monomeric or oligomeric silicic acids could provide information about the mechanisms.

The reactivity of monomeric silicic acids was first investigated by Brintzinger and Troemer in 1929 [33]. They developed membrane separation techniques for determining monomeric, dimeric and higher oligomeric silicic acids. The monomeric acid was prepared by introducing  $\text{Si}(\text{OR})_4$  or  $\text{SiCl}_4$  vapour into water. Their results show differences in the stability of silicic acid as a function of the preparation. Under certain reaction conditions monomeric and dimeric acids are stable for hours. Measurements of condensation rates as a function of the pH value have been published by Schwarz et al. [32] and Alexander [34]. Both authors could establish a minimum of the condensation rate at a pH value of about 3. There is an agreement with the results of Iler

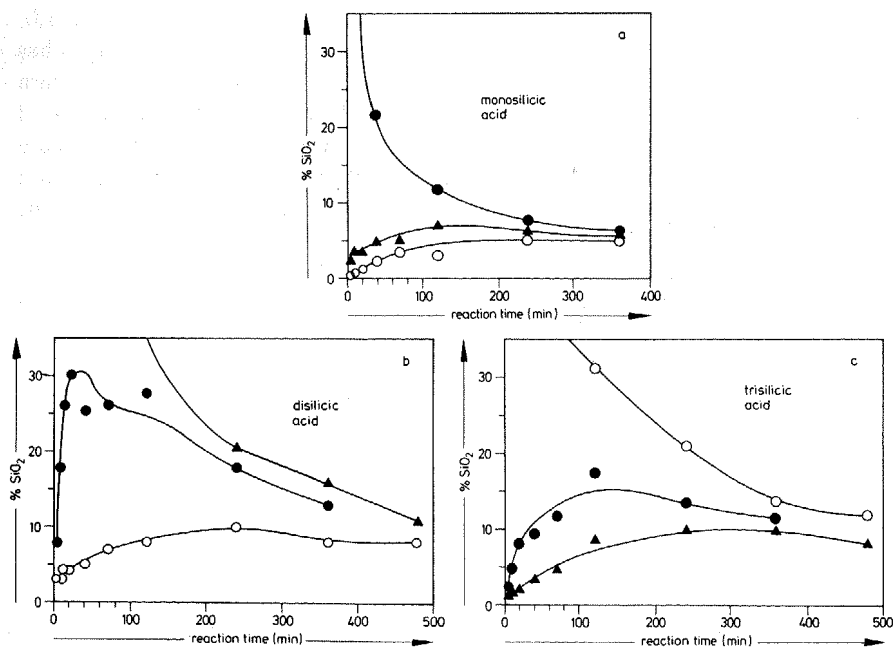


Fig. 1a-c. Distribution curves of mono(●)-, di(▲)-, and tri(○)silicic acids as a function of time and starting acid after measurements and plots by Hoebbel et al. [36].

[11], who measured the gelling time of aqueous solutions of monosilicic acid and found a minimum at a pH value of about 6. Okkerse [26] found basic differences in condensation kinetics as a function of the pH values ( $\text{pH} < 2 \equiv 3\text{rd}$  order and  $\text{pH} > 2 \equiv 2\text{nd}$  order reaction for the disappearance of monomers). The results are explained on the basis that three-silicon transition intermediates are formed at  $\text{pH} < 2$  and two-silicon intermediates are formed at  $\text{pH} > 2$ . Extensive considerations about the theoretical possibilities of particle growth have been given by Iler. At first cyclic and then three-dimensional particle growth mechanisms were made probable [11].

Recently more sophisticated investigations were presented by Engelhardt et al. [35] and Hoebbel et al. [36] using  $^{29}\text{Si}$  NMR spectroscopy. The monomeric silicic acid was prepared by hydrolysis of alkoxy silanes. Fig. 1a–c shows the reaction of some silicic acids as obtained by NMR according to ref. 36.

It is very interesting that the polycondensation process involves well defined stages, as di-, tri-, tetra-, and cyclotetrameric species; no branched species were observed at lower degrees of polymerization. This relates to results obtained by partial hydrolysis in alcoholic solution.

Summarizing the results of the discussed papers it can be said that a lot of mechanistic details are given which may help to interpret reaction paths in the sol–gel process.

## 2.2. Hydrolysis mechanism

The interest in the mechanisms of the hydrolysis of tetra-alkoxy silanes has increased parallel to the evaluation of mechanistic consideration in modern organic chemistry. To the extent that models for the reaction at the C–O–bond were developed, investigations were carried out to prove how these models are transferable to the Si–O–bond. Reviews from Post [37], Andrianov [38] and Voronkov et al. [30] give an excellent survey over the wide field. From the standpoint of preparing materials, it is of interest to know something about the rate of hydrolysis and condensation to oligomers and polymers, especially if intermediates are of importance for practical use. A strong influence of the ligands on  $\text{Si}(\text{OR})_4$  hydrolysis rate can be expected, as known from carbon chemistry. Moreover, the influence of the catalyst, in most cases  $\text{H}^+$ , is important. Furthermore, the question of the molecular mechanism arises. In carbon chemistry hydrolysis of orthoesters usually follows a dissociative mechanism with a carbonium ion as intermediate to be postulated.

The influence of alkyl radicals on the hydrolysis rate of tetra-alkoxy silanes was investigated by Aelion et al. [27]. Table 1 shows some results of their experiments.

It was shown that the rate constants of the proton-catalyzed hydrolysis decrease significantly with increasing chain length of R. In the case of the acid catalyzed reaction they found an influence of the catalyst concentration on the rate constants and even on the equilibrium constants of the reaction. Thus, for the rate constant of tetra-alkoxy silane hydrolysis in dioxane and methanol with

Table 1

Rate constants for acid hydrolysis of different alkoxy silanes [27]

Rate constants  $k$  for acid hydrolysis of tetra-alkoxy silanes  $(RO)_4Si$  at 20°C

R	$k$ $10^2(\text{l mol}^{-1} \text{s}^{-1} [\text{H}^+]^{-1})$
$\text{C}_2\text{H}_5$	5.1
$\text{C}_4\text{H}_9$	1.9
$\text{C}_6\text{H}_{13}$	0.83
$(\text{CH}_3)_2\text{CH}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{CH}_2$	0.30

Rate constants  $k$  ( $10^2 (\text{l mol}^{-1} \text{s}^{-1} [\text{H}^+]^{-1})$ ) for acid hydrolysis of alkoxyethoxy silanes  $(RO)_{4-n}\text{Si}(\text{OC}_2\text{H}_5)_n$  at 20°C

n	R			
	$\text{C}_6\text{H}_{13}$	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2$ H <sub>3</sub> C-CH	$\text{CH}_3(\text{CH}_2)_5$ H <sub>3</sub> C-CH	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2$ CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> -CH
0	0.8	-	-	0.030
1	1.1	-	-	-
2	5.0	0.15	0.095	0.038
3	5.0	-	-	-

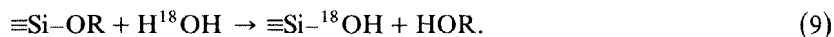
diluted HCl they found:

$$\log k = \log H^+ + \log 0.0059. \quad (8)$$

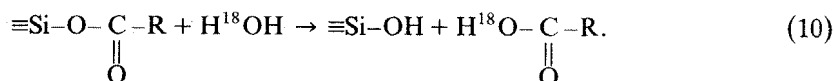
The dependence of both constants on  $H^+$  concentration cannot be simply explained.

The existence of an equilibrium in the hydrolysis reaction of  $\text{Si}(\text{OR})_4$  in alcohol could be established by our own investigations, too, but in contrary to the results of Aelion we did not find the equilibrium constant depending on proton concentration. This checks with the consideration of only a catalytic role for  $H^+$ .

While Aelion tried to explain his kinetic results by the postulation of a penta- or hexacoordinated silicon transition complex, Khaskin in 1952 [39] showed that the hydrolysis of silicoorthoesters both in the acid and alkaline medium follows eq. (9), as  $^{18}\text{O}$  experiments proved:



In opposition to that in acyloxides the  $-\text{O}-\text{C}$ -bond is cleaved:



According to eq. (9) the formation of a trivalent siliconium ion as transition state and therefore the formation of this ion as rate limiting step of the hydrolysis was postulated [40].

### 3. Hydrolysis and condensation of organoalkoxysilanes

If mechanisms are considered, one advantage of organoalkoxysilanes is the possibility to study the reaction of two or even one OR group in one ester molecule, e.g.:



Of course the influence of R' on the reaction has to be taken into account. On the other hand there is the possibility to synthesize optically active compounds and to study the change of conformation during hydrolysis.

By analogy to the silicoorthoesters the chemistry of organoalkoxysilanes has a long history, too: the first to describe the hydrolysis and condensation of organoalkoxysilanes was Ladenburg in 1874 [41]. He received polyalkylsiloxane polymers by saponification of diethyldichlorosilane or diethyldiethoxysilane.

In the past 100 years an innumerable number of papers have been published concerning organoalkoxysilanes or their reaction products. The investigations were carried out for different reasons: Kipping synthesized numerous new siloxanes and analyzed the reaction products [42]. He was the first one who proved structures of polyorganosiloxanes and who disclosed that the  $\equiv Si-O-Si \equiv$  grouping differs from the  $\equiv C-O-C \equiv$  grouping in its reactivity. The most work published in connection with organoalkoxysilanes is concerned with the production of silicones, but there the properties of the obtained products were more interesting than mechanistic details [43].

Concerning mechanisms, detailed work was carried out by Sommer et al. [44,45] with optically active compounds. Thus, as a function of reaction conditions of the hydrolysis of compounds of the type  $R'_3Si^*X$  ( $X = OR, Cl$ ), the conformation was kept up, changed or racemisation took place. Especially the hydrolysis of  $R'_3Si^*OR$  in acetone did not lead to racemisation, indicating that no siliconium ion was present. This checks with results of Swain [40]. Investigations of Khaskin [39] show the incorporation of  $^{18}O$  in the hydrolysis of  $(CH_3)_2Si(OR)_2$  from  $H^{18}OH$ , but unfortunately no correlation is possible between the results of Khaskin and Sommer.

Investigations of the hydrolysis were made by Andrianov [38], indicating that in the acid catalyzed reaction, the presence of nonhydrolyzable radicals leads to higher hydrolysis rates. This behaviour checks with results of Åkerman [46] and is important, if organoalkoxysilanes should be crosslinked with tetra-alkoxysilanes. In our own investigations we synthesized copolymers from  $(CH_3)_2Si(OC_2H_5)_2$  and  $Si(OC_2H_5)_4$ . In order to obtain data on hydrolysis rates, different alkoxysilanes were investigated under different conditions by an IR method [28,47]. Figs. 2a and b show the disappearance of the monomers with time (HCl or  $NH_3$  catalysis). In the case of the orthoesters, both HCl and  $NH_3$  affect hydrolysis. In the case of dimethyldiethoxysilane and trimethylethoxysilane no hydrolysis could be observed, even if the  $NH_3$  concentration was increased up to 5 mol./l. With HCl, the  $CH_3$ -substituted silanes react



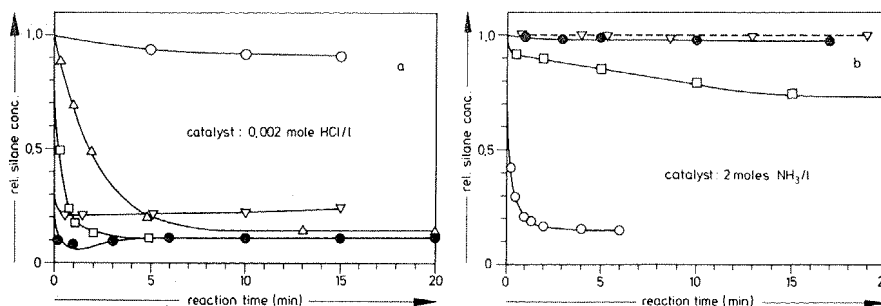


Fig. 2. Hydrolysis of different silanes in ethanol as solvent (volume ratio 1: 1); ●: (CH<sub>3</sub>)<sub>3</sub>SiOC<sub>2</sub>H<sub>5</sub>; ▽: (CH<sub>3</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>; □: CH<sub>3</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>; ○: Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>; △: Si(OCH<sub>3</sub>)<sub>4</sub>.

significantly faster than the orthoesters. The acceleration in H<sup>+</sup> catalysis becomes understandable, if for the rate-limiting step the formation of a siliconium ion of the type RO(CH<sub>3</sub>)<sub>2</sub>Si<sup>+</sup> or (CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup> will be postulated, since then complex stabilization will be affected by the +I-effect of the alkyl radicals. In the case of NH<sub>3</sub> catalysis, there must be different mechanisms between the orthoesters and the alkyl substituted esters: it was experimentally proved that the orthoesters show increasing hydrolysis rates with increasing NH<sub>3</sub> concentrations, whereas the substituted esters show the opposite behaviour, and with concentrations of 2 mol. NH<sub>3</sub>/l the rates become almost zero. Steric hindrance or the lowering of the positive charge at the silicon due to +I-ligands and therefore a nucleophilic attack becoming more difficult may be taken into account as explanations, but more mechanistic details have to be evaluated in this case. As far as the co-condensation of (CH<sub>3</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> is concerned, H<sup>+</sup> catalysis has to be preferred, since by this reactive monomers from both are able to be produced and condensed to a polymer.

#### 4. Conclusions

The basic principles of hydrolysis and condensation of alkoxy-silanes have been well-known for a long time, but they have been used for preparing glasses and glass ceramics by the sol-gel process for only a short period. Investigations of hydrolysis and condensation mechanisms of alkoxy- and organoalkoxy-silanes show that under well defined conditions detailed statements about kinetics and mechanisms can be pronounced, but it is still difficult to make general forecastings with respect to the influence of composition and reaction parameters on the material properties. Much information about the behaviour of alkoxy-silanes can be found in the literature and they may be helpful for the sol-gel process. Since it was not possible to review these interesting results in

detail in the present paper, the reader may find more information from the genuine contributions.

## References

- [1] H. Dislich, *Angew. Chem.* 83 (1971) 428.
- [2] R. Roy, *J. Amer. Ceram. Soc.* 52 (1969) 344.
- [3] K.S. Mazdiyasi, R.T. Dolloff and J.S. Smith, II, *J. Amer. Ceram. Soc.* 52 (1969) 523.
- [4] S.P. Mukherjee and J. Zarzycki, *J. Mater. Sci.* 11 (1976) 341.
- [5] B.E. Yoldas, *J. Mater. Sci.* 12 (1977) 1203.
- [6] K. Kamiya and S. Sakka, *Res. Rep. Fac. Eng. Mie Univ.* 2 (1977) 87.
- [7] M. Nogami and Y. Moriya, *J. Non-Crystalline Solids* 37 (1980) 191.
- [8] G. Carturan, V. Gottardi and M. Graziani, *J. Non-Crystalline Solids* 29 (1978) 41.
- [9] S. Sakka and K. Kamiya, *J. Non-Crystalline Solids* 43 (1980) 403.
- [10] J.D. Mackenzie, *J. Non-Crystalline Solids* 48 (1981) 1.
- [11] R.K. Iler, *The chemistry of silica* (Wiley, New York, 1979).
- [12] D.P. Partlow and B.E. Yoldas, *J. Non-Crystalline Solids* 46 (1981) 153.
- [13] Ebelmen, *Ann.* 57 (1846) 319.
- [14] C. Friedel and A. Ladenburg, *Ann.* 143 (1867) 118.
- [15] C. Friedel and J. Crafts, *Ann.* 136 (1865) 203.
- [16] C. Friedel and A. Ladenburg, *Ann.* 145 (1868) 179.
- [17] E. Konrad, O. Bächle and R. Singer, *Ann.* 474 (1929) 276.
- [18] M.F. Bechtold, R.D. Vest and L.P. Plambeck Jr, *J. Amer. Chem. Soc.* 90 (1968) 4590.
- [19] S. Sakka and K. Kamiya, *J. Non-Crystalline Solids* 48 (1982) 31.
- [20] B.E. Yoldas, *J. Non-Crystalline Solids* 51 (1982) 105.
- [21] K.K. Unger, *Porous silica. J. Chromatography Library*, Vol. 16 (Elsevier, Amsterdam, 1979).
- [22] C.J. Brinker, K.D. Keefer, D.W. Schaefer and C.S. Ashley, *J. Non-Crystalline Solids* 48 (1982) 47.
- [23] J. Zarzycki, *Ibid.*, 105.
- [24] B.W. Peace, K.G. Mayhan and J.F. Month, *Polymer* 14 (1973) 420.
- [25] W.A. Weyl, *Miner. Ind. Exp. Stn. Bull.* 57 (1951) 56.
- [26] C. Okkerse, in: *Physical and chemical aspects of adsorbents and catalysts*, ed., B.G. Linsen (Academic Press, New York, 1970).
- [27] R. Aelion, A. Loebel and F. Eirich, *J. Amer. Chem. Soc.* 72 (1950) 5705.
- [28] H. Schmidt and A. Kaiser, *Glastechn. Ber.* 54 (1981) 338.
- [29] W. Noll, *Chemie und Technologie der Silicone*, 2. Auflage (Verlag Chemie, Weinheim, 1968).
- [30] M.G. Voronkov, V.P. Mileshevich and Y.A. Yuzhevskii, *The Siloxane Bond* (Plenum, New York, London, 1978).
- [31] R. Schwarz and A. Kessler, *Z. anorg. allg. Chem.* 263 (1959) 15.
- [32] R. Schwarz and K.G. Knauff, *Z. anorg. allg. Chem.* 275 (1954) 176.
- [33] H. Brintzinger and B. Troemer, *Z. anorg. allg. Chem.* 181 (1929) 237.
- [34] G.B. Alexander, *J. Amer. Chem. Soc.* 76 (1954) 2994.
- [35] G. Engelhardt, W. Altenburg, D. Hoebbel and W. Wieker, *Z. anorg. allg. Chem.* 428 (1977) 43.
- [36] D. Hoebbel, G. Garzó, G. Engelhardt and A. Till, *Z. anorg. allg. Chem.* 450 (1979) 5.
- [37] H.W. Post, *The chemistry of the aliphatic orthoesters* (Reinhold, New York, 1943).
- [38] K.A. Andrianov, *Organic silicon compounds* (State Sci. Publ. House for Chemical Literature, Moscow, 1955).
- [39] I.G. Khaskin, *Dokl. Akad. Nauk SSSR* 85 (1952) 129.
- [40] C.G. Swain, R.M. Esteve Jr and R.H. Jones, *J. Amer. Chem. Soc.* 71 (1949) 965.
- [41] A. Ladenburg, *Ann.* 173 (1874) 143.

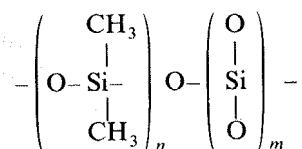
- [42] F.S. Kipping and J.T. Abrams, *J. Chem. Soc.* (1944) 81.  
 [43] E.G. Rochow, *An introduction to the chemistry of the silicones* (Wiley, New York, 1951).  
 [44] L.H. Sommer, C.F. Frye, M.C. Muslof, G.A. Parker, P.G. Rodewald, K.W. Michael, Y. Okaya and P. Pepinski, *J. Amer. Chem. Soc.* 83 (1961) 2210.  
 [45] L.H. Sommer and C.F. Frye, *J. Amer. Chem. Soc.* 82 (1960) 3796.  
 [46] E. Åkerman, *Acta Chem. Scand.* 10 (1956) 298; 11 (1957) 298.  
 [47] H. Schmidt, H. Scholze and A. Kaiser, *J. Non-Crystalline Solids* 48 (1981) 65.

### Discussion

This paper aroused much interest and more detail was asked on the different hydrolysis mechanisms of the acid- and base-catalyzed hydrolysis of alkylalkoxy compounds. The  $H^+$  catalyzed hydrolysis reaction shows differences in the reaction rate between  $(CH_3)_2Si(OC_2H_5)_2$  (I) and  $Si(OC_2H_5)_4$  (II) compounds. The much faster reaction of I may be due to the +I-effect of the  $-CH_3$  radicals and becomes understandable if the formation of  $\equiv Si^+$  (siliconium) ions is postulated as the rate determining step. The +I-effect will reduce the actual positive charge of a siliconium ion on the one side and favor the attack of a proton on the Si-O-R on the other side. In the same way, the nucleophilic attack on the Si will become more difficult in the base-catalyzed case. More experiments are, however, needed to prove this.

The possibilities of applications of these concepts to the synthesis of mixed organic-inorganic materials were also discussed.

In the prepared polymers, of the general form:



the first group is a linearly polymerizing component and the second a three-dimensional one. In this way it is possible to prepare materials with specific microstructures tailored to specific needs, e.g. soft abrasives.