THERMOGRAVIMETRIC STUDY OF THE KINETICS OF STRUCTURAL RELAXATION OF AMORPHOUS SILICA

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To determine the role of the forms of fixed water in the relaxation of the silica structure, silica was treated with hot water vapour in an autoclave, and the kinetics of its dehydration were studied by thermogravimetry. Five successive stages of relaxation were established:

1. Flocculation of globules, accompanied by evaporation of the polymolecular water layer situated in the interglobular space.
2. Formation of a glassy structure, accompanied by further water evaporation.
3. Transition of the glassy structure to cristobalite with the formation of large particles.
4. Formation of quartz seeds within each particle.
5. Aggregation of oriented seeds into monocrystals of quartz.

The crystallization of amorphous silica in all stages depends on the interaction of different water forms with fragments of the silicon-oxygen skeleton.

The activation energy of water evaporation was calculated; it varies from 21 to 38 kJ/mol for the different stages of the process. The activation energy of silica relaxation was evaluated to be about 125 kJ/mol.

Amorphous silica is a widespread material utilized in various branches of industry. Its characteristic feature is its globular structure: particles of silica are composed of globules — curved macromolecules, varying from 50 to several thousand Angstroms in size. On the surface the globules are covered with hydroxy groups the bulk volume being composed of chaotic silicon-oxygen tetrahedra, incorporating several hydroxy groups which escaped reaction, and water molecules resulting from the polycondensation of silicic acid. The high thermal resistance of water-free silica depends on the durability of the siloxane bonding (about 459 kJ/mol). On the other hand, the presence of residual hydroxy groups, interglobular liquid and intraglobular water leads to a possibility of changes in the structure of silica, which is not stable, but tends to relaxation — a spontaneous transition to a more thermodynamically stable state. A very slow relaxation goes on even at room temperature and atmospheric pressure and is known as the ageing of silica. Rising temperature up to 900—1000° without contact with vapour leads to the dehydration of silica, this process resulting in a more stable structure. At this temperature the mobility of the silicon-oxygen tetrahedra increases significantly and the residual hydroxy groups migrate, condensing and evolving water; the surface of the silica also decreases. Contact with water vapour significantly increases the lability of the

siloxane bonding and evident changes in the structure of silica may already be observed at 150°. The final product of relaxation is quartz. Depending on the temperature and vapour regime, there may be great variance in the structure of silica. For example, finely porous silica gel may produce in a series materials such as coarsely globular silica gel, glassy silica, cristobalite and quartz.

The relaxation of the silica structure is a complex multistage process, the kinetics and expression of which depend on the form of the fixed water. Earlier publications [1] report the thermal effects of dehydration at temperatures in the range of 100, 350 and 500° as being 41.8, 20.9 and 4.2 kJ/mol, respectively. These were determined by a thermogravimetric study of the thermodynamics of silica dehydration. On the basis three forms of fixed water were identified: a polymolecular layer of water in the interglobular space; water molecules linked through hydrogen with the silanol or siloxane groups inside the globules; water molecules coordinated to silicon atoms. To determine the role of the form of the fixed water in the relaxation of the silica structure, silica was treated with hot water vapour and the kinetics of its dehydration were studied by thermogravimetry. The utilized silica was obtained through ammonia hydrolysis of tetraethoxysilane. The treatment was carried out in an autoclave at a temperature of 400 − 450° with a water content of 1.5 − 30% in the volume of the autoclave. Figure 1 shows the curves of weight loss of the original silica heated to 1000° and the samples of silica after treatment with hot water vapour at 450°. The TG curves for the original silica clearly show two weight loss intervals, from 60 to 200° and from 350 to 650°. At higher temperature the TG curve is practically parallel to the abscissa. In the first temperature interval the dehydration is accompanied by a thermal effect in the DTA curve. In the second interval no thermal effect was observed for any the samples. During the hot water vapour treatment there was a significant decrease in the amount of the first form of water evaporating at 60 to 200° during the first two hours and it totally disappeared in three hours. The second water form, evaporating at 350 to 650°, disappeared only after 60 hours of hot water vapour treatment, when the amorphous silica had turned wholly into quartz.

Figure 1 shows the correlation of the total amount of water evaporated when the silica was heated to 1000° with the duration of the treatment. The curve includes the results of the thermogravimetric treatment. Different forms of silica were identified by the appearance of thermal effects at the transitional stages in the DTA curves.

The data obtained were compared with the results of X-ray analysis, IR spectroscopic and electron microscopic analyses. To classify the forms of water and their role in the hot water vapour treatment, the activation energy of water evaporation in different temperature intervals was determined.

The activation energy of evaporation of the first water form is conjugate to the thermal effect of dehydration. The evaporation of the second water form at 350 to 650° is not accompanied by thermal effects and the results of differential thermal analysis of these samples lead to no conclusion on the properties of this water form. IR spectroscopy showed that in all the spectra of silica samples treated
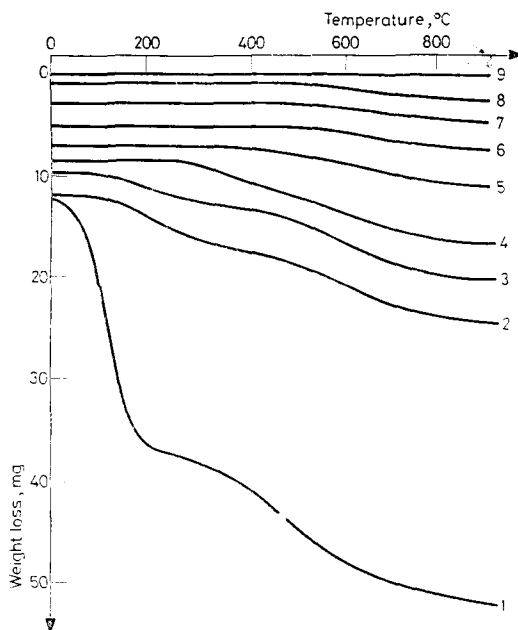
Fig. 1. Curves of weight loss of different samples of silica: original (1) and treated with hot vapour at 450 °C: 2 — 2 hours, 3 — 3 hours, 4 — 7 hours, 5 — 18 hours, 6 — 28 hours, 7 — 44 hours, 8 — 50 hours, 9 — 64 hours

with hot water vapour the 1640 cm^{-1} band corresponding to the deformation oscillations of water molecules was present; the 960 cm^{-1} band corresponding to the deformation oscillations of free hydroxy groups was absent and satisfactorily defined bands were present at 3200 cm^{-1}, 3450 cm^{-1}, and 3680 cm^{-1}, corresponding to the oscillations of hydroxy groups disturbed by hydrogen bonding. These data testify to the presence of fixed water molecules in the structure of silica (besides hydroxy groups), but the data are not comprehensive enough to identify the distribution or energy characteristics of these molecules. Determination of the activation energy of water evaporation, especially in the 350 to 650° interval, was quite significant as regards obtaining these data. Reich's method was used in the kinetics study [2] it was assumed that water evaporation is a first-order reaction. The activation energy of evaporation was calculated from the formula:

$$E = \frac{\Delta \ln \ln \frac{W_0}{W_t} \cdot R}{\Delta \frac{1}{T}}$$

where: W_t = sample weight at temperature T;
W_0 = sample weight at the temperature of the beginning of dehydration.

Table 1

Duration of treatment, hours	Interval	E, kJ/mol	ΔH, kJ/mol H_2O
0	60—200	36.8±1.2	38.4 ± 2.1
	350—650	28.0±1.2	
1	60—200	36.3±0.8	
	350—650	27.2±0.8	
2	350—650	20.9±0.4	
8	350—650	20.9±0.4	
50	350—650	20.9±0.8	

Table 1 shows the thermal effect of dehydration (1) and the activation energy of water evaporation depending on the duration of treatment with hot water vapour. The Table and Fig. 1 show that in the studied samples two forms of water may be identified. For first form: the temperature interval of dehydration = 60— 200° the enthalpy of dehydration = 38−42 kJ/mol, and the activation energy of evaporation = 36−38 kJ/mol.

This is mostly a polymolecular water layer in the interglobular space. The water evaporating in this interval may include other water forms with lower values of enthalpy and activation energy of evaporation. However, these parameters, being close to those of pure water, show that in the discussed case mostly the evaporation of water molecules from the polymolecular layer takes place. For the second form: the temperature interval of dehydration = 350−650° there is no thermal effect, and the activation energy of evaporation = 21−29 kJ/mol. These are mostly water molecules attached through hydrogen bonds to fragments of the silicon-oxygen lattice. The integral flow may include a certain amount of water coordinated to silicon atoms. The absence of other evaporating substances apart from water was checked by means of mass spectrometry.

It is notable that the values of the thermal effect of dehydration and the activation energy of evaporation correspond to the integral effect of the simultaneous evaporation of the different water forms. For example, if the silica surface contains water molecules attached through water bonds to the surface hydroxy groups the values of the enthalpy and activation energy of evaporation may be somewhat lower than the corresponding values for water. In the second temperature interval the presence of water coordinated to silicon atoms results in a decrease in the activation energy of evaporation to ∼21 kJ/mol for a longer duration of hot water vapour treatment.

Figure 2 presents a curve of the variations in the total water content of the silica depending on the duration of hot water vapour treatment. From this curve it is evident that during the first ten hours there is a sharp decrease in the content of water, from 7 to 0.4%. According to optical and electron microscopy, there is also a significant increase in the size of the globules, from 50 Å to 10 000 Å. As a
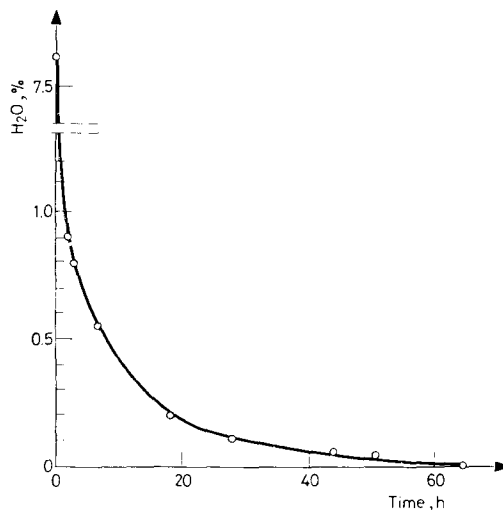

Fig. 2. The correlation of the total water content evaporated at up to 1000 °C with the duration of hot vapour treatment at 450 °C, 3 % of water in the volume of the autoclave

result large globules form which are the basis for the large irregular lumps clearly seen under the optical microscope. The increase in size of the globules is accompanied by the disappearance from the TG and DTA curves of the effects corresponding to the dehydration of the first form of water, and also by the disappearance from the IR spectrum of the 960 cm^{-1} band, corresponding to the deformation oscillations of the surface hydroxy groups.

This leads to the conclusion that the first stage of relaxation the increase in size of the globules — relies on the polymolecular layer in the interglobular space. The size of the globules increases through coalescence (merging of drops). The rate of the process is determined by the surface diffusion of the silicon-oxygen tetrahedra, which in turn depends on the number of silanol groups on the surface of the globules and on the properties of the interglobular liquid.

When the treatment lasts 10 to 64 hours, the total water content varies insignificantly, from 0.4% to absolute zero within the sensitivity range of the apparatus. During this time the following stages may be observed in the relaxation of the silica structure:

1. Flocculation of globules and the formation of spherical polyglobular particles 0.02—0.15 cm in diameter, disconnected from each other. The water content is

0.2%, and the particle density 2.15−2.19. The flocculation is ended after 32 hours of the hot water vapour treatment.

2. Changes in the structure of the floccules, their density increasing to 2.28, which corresponds to the density of quartz glass. The water content decreases to 0.1%. The process is ended after 50 hours of the hot water vapour treatment.

3. Conversion of the glassy structure to the structure of cristobalite, with simultaneous aggregation of the particles into large irregular lumps up to 1 mm in size. The water content is at the limit of the apparatus sensitivity. The density is 2.33. The process is ended after 55 hours of treatment.

4. Formation of quartz seeds within each particle, the limits of which are easily seen in the microscope. Due to the action of the surface forces, these seeds are oriented along a definite axis. Depending on the stage of the process, the density varies from 2.33 to 2.66. No weight loss is registered by the derivatograph.

5. Aggregation of oriented seeds into monocrystals of quartz. Under these conditions the relaxation is ended after 64 hours.

Table 2

Duration of treatment, hours	Water volume, weight %	Structure	Density, g/cm³
10	0.4	amorphous	2.09±0.05
10−32	0.1	glassy	2.23±0.05
32−44	0.05	cristobalite	2.33±0.05
44−62	0.05−0	quartz	2.66±0.05

Digital data on the process are given in Table 2. They describe the changes in the silica structure in the course of hot water vapour treatment as a process depending on the interaction of the different water forms with fragments of the silicon-oxygen lattice. The first portion of the kinetic curve (Fig. 2, 0−10 hours) reflects the dominating influence of the interaction of surface silanol groups with the polymolecular water layer from the interglobular space. This stage of relaxation ends when a critical size of globules (1 mcm) is reached. Further stages in the structure of silica are determined by the presence of interglobular water attached through hydrogen and coordination bonds to the silicon-oxygen tetrahedra. The conditions of the hot water vapour treatment exclude the unequal evolution of water with the preservation of the chaotic distribution of the silicon-oxygen tetrahedra. The evolution of water is directly correlated with the formation of a more stable silica structure and results from the redistribution of the siloxane bonds. The high mobility of the water molecules at higher temperature and pressure entails the disruption of the siloxane bonds and the formation of intraglobular hydroxy groups the latter entering into reaction with each other. As a result of this reaction water is detached and new siloxane bonds appear, the distribution of which corresponds to a more thermodynamically stable state of the silica.

To evaluate the kinetic parameters of relaxation, use was made of the curves showing the correlation of the total water content with the duration of hot water vapour treatment of amorphous silica at 400—450° (Fig. 3). Though a general
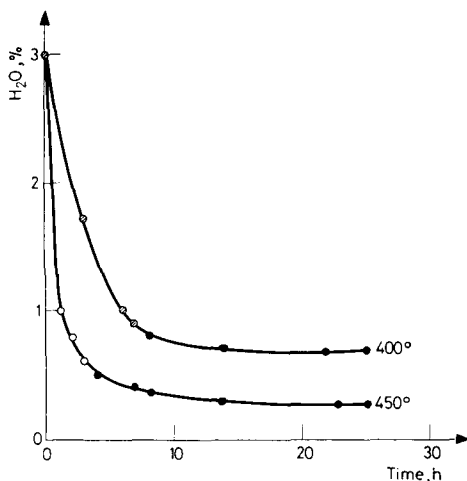

Fig. 3. The correlation of the total water content with the duration of the hot vapour treatment, 1.5% water in the volume of the autoclave: ● — samples with quartz

correlation may be observed between the residual water content and the stage of relaxation, direct thematic processing of the curves does not seem justified as the process is very complex and multistage. The appearance of the quartz effect in the DTA curves was chosen for estimation of the activation energy of silica relaxation.

Assuming that the kinetics of the changes in the silica structure may be described by an equation of the first degree, these may be represented as follows:

$$\frac{dW}{dt} = K_0 e^{-E/RT}$$

where: W = sample weight at temperature T.
After integration the equation is transformed as follows:

$$\ln \frac{W_0}{W_t} = K_0 e^{-E/RT} t.$$

Assuming $t_0 = 0$, the equation is converted as follows:

$$\ln \frac{W_0}{W_t} = K_0 e^{-E/RT} t.$$

From the curves constructed at different temperature levels, the points representing the appearance of the quartz effect were chosen and the correlation of the activation energy of the structural changes with the duration of relaxation was obtained, assuming that the finalty of the process for these points was the same:

$$\ln \frac{t_0}{t} = -\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

from which

$$E = \frac{\ln t_0/t \cdot R}{\dfrac{1}{T_2} - \dfrac{1}{T_1}}.$$

The activation energy thus obtained was 125 kJ/mol. This value is generally characteristic of the diffusion processes, which fact supports the assumption that the relaxation of silica is determined by the diffusion of the silicon-oxygen tetrahedra.

References

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ZUSAMMENFASSUNG — Zur Bestimmung der Rolle der Formen des gebundenen Wassers bei der Relaxation der Silikatstruktur wurde das Kieselerde in einem Autoklaven mit heissem Wasserdampf behandelt und die Kinetik seiner Dehydratisierung thermogravimetrisch untersucht. Fünf aufeinanderfolgende Etappen der Relaxation wurden festgestellt:

1. Flockenbildung von kugelförmigen Partikeln, begleitet von dem Verdampfen der polymolekularen, im interglobulären Raum befindlichen Wasserschicht.
2. Bildung einer Glasstruktur, begleitet durch weitere Wasserverdampfung.
3. Übergang der Glasstruktur in Cristobalith, unter Bildung grosser Partikel.
4. Bildung von Quarzkörnchen innerhalb der einzelnen Partikel.
5. Aggregation der orientierten Körnchen zu Quarz-Einkristallen.

Die Kristallisation von amorpher Kieselerde hängt in allen Stadien von der Wechselwirkung der verschiedenen Wasserformen mit den Fragmenten des Silizium-Sauerstoff-Skellets ab.

Die Aktivierungsenergie der Wasserverdampfung wurde berechnet; sie variiert zwischen 21 und 38 kJ/mol für die verschiedenen Stufen des Vorgangs. Die Aktivierungsenergie der Silikatrelaxation wurde als etwa 125 kJ/mol bewertet.

Резюме — С целью выявления роли различных форм связанной воды в процессе релаксации структуры кремнезёма проведено термогравиметрическое исследование кинетики дегидратации кремнезёма, подвергнутого термопаровой обработке в автоклаве. Найдены

5 последовательных стадий релаксации: 1 — флокуляция глобул, сопровождающаяся испарением полимолекулярного слоя воды, находящейся в межглобулярном пространстве; 2 — образование стеклообразной структуры с дальнейшим выделением воды; 3 — переход стеклообразной структуры в кристобалит с образованием крупных частиц; 4 — образование внутри частиц зародышей кварца; 5 — объединение зародышей в кварцевые монокристаллы.

Кристаллизация аморфного кремнезёма на всех стадиях определяется взаимодействием различный форм воды с фрагментами кремнекислородного скелета.

Вычислена энергия активации испарения, которая изменяется от 21 до 38 кдж/моль для различных стадий процесса, о оценена энергия активации процесса релаксации, составляющая около 125 кдж/моль.