THERMAL CHANGES OF AMORPHOUS SiO$_2$ AS A CONSEQUENCE OF A PRECIPITATION TEMPERATURE

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Abstract

Amorphous precipitate SiO$_2$ as a subject of this research is obtained by reaction between Na-silicate, water solution (water glass) and sulphuric acid. The influence of precipitation temperature, upon the characteristics of obtained samples is analysed. The temperature is chosen as a parameter, which has a strong influence upon the structure and characteristics of a product, but it has a very narrow interval at the same time, where the precipitation process under an atmospheric pressure is possible. Some more important characteristics of the samples, obtained at $80 - 95\,°C$ (values close to the limits of temperature interval where the precipitation reaction is possible), were analysed to show the essential differences, caused by the temperature. The analysis referred to determination of the dimensions of primary and secondary particles, density, specific surface area, and level of amorphous state (all this in green state). Then, the morphological and structural changes during heating at the characteristic temperature are followed. The changes are determined by the above characteristics and also by measuring the energetic values of some of them. Significant differences are noticed between samples where the higher precipitation temperature points to obtaining of amorphous precipitate with bigger primary particles, less specific surface area, higher density and higher molecular order which is manifested through faster and easier crystallization (when heating at $1100\,°C$).

Keywords: amorphous SiO$_2$, precipitation temperature, agglomeration, specific surface area, thermal stability.

1. Introduction

The process of obtaining amorphous SiO$_2$ precipitate from hydrated Na-silicate (water glass) can occur by neutralization with HCl, H$_2$SO$_4$ and some other acids. During the precipitation by HCl (one of the most usual methods) it is necessary to use an additive and after the product is obtained, a necessary calcination follows, due to the increasing specific surface area [1]. To avoid the simultaneous influence of more factors upon the reaction system, the sulphuric acid is chosen, by which an amorphous SiO$_2$ precipitate with a larger specific surface area can be obtained without using additives. The ratio SiO$_2$/Na$_2$O in water glass is 2.8.

In general, the obtained precipitate is formed of agglomerated particles, which consist of more aggregates, and these latter ones of even finer primary particles [2]. The dimensions of these particles are only few nanometers, their aggregates few tens

nanometers and the agglomerates are of micrometer dimensions. These systems are of fractal nature [3, 4, 5].

Thus, we can produce amorphous SiO_2 precipitate with different morphology and properties [6], and these properties would depend on the conditions of precipitation (temperature, pH value, the concentration of the components e.t.c.). The thermal stability [7, 8] is one of the most important characteristics, which also depends on the created structure in the stage of precipitation.

2. Experimental

An important characteristic of the experiments performed is that the precipitate is obtained in variable pH area, that is from higher to lower value of the medium. In such cases the obtained primary precipitate (pH$\sim$11.5) is subject to significant changes concerning the morphology and molecular order, during the further reduction of the pH value in the reaction system.

The reaction temperature has also an essential influence upon the properties of the precipitate. It must be between approximately 80 to approximately 95 °C, because there is no solid state of the SiO_2 precipitate, but gel stage at temperature lower than 75 °C. The highest experimental temperature is limited to 95 °C because the boiling point of reaction mixture at normal pressure is very close to this temperature.

In such a system there is a simultaneous effect of pH value and the temperature upon the product properties, and because of that, different samples are made at different temperature values (80 − 95 °C) and final pH = 1, as a constant parameter value.

Although there is a continuous transition of the changes in the structure and the properties of the samples obtained in the interval where the temperature varies, the limit values of this parameter are taken for better emphasizing the differences between the properties of the products obtained.

3. Results

The essential difference between the sample properties lies in the different morphology of the particles and the different level of the structural (molecular) order.

The sample obtained at 95 °C and the final pH = 1 (with a period of stabilization of 15 min) is shown in *Fig. 1*. It is obvious that average approximate diameter of the least visible particles is 50 nm. The calculated specific surface area of this sample is 56.23 m^2/g, while the measured specific surface area by BET is 312 m^2/g. According to this, particles of approximately 50 nm are actually aggregates of only few nanometers particles, and these particles create agglomerates of micrometer dimensions. The average diameter of the agglomerates taken from granulometric

analysis is 21 μm. (Fritsch Particle Sizer – Analysette 22). The density of this sample is 2.134 g/cm^3.

The sample obtained at 80 °C and a final pH $= 1$ (with period of stabilization of 15 min) is shown in *Fig. 2*. Here, the least visible particles have a diameter of 33 nm and a specific surface area of 465 m^2/g, while if calculated, the specific surface area for spherical of 33 nm particles is 85.97 m^2/g. The conspicuously lower value points to the fact that here, also, these particles are aggregates of only few nanometer particles. The measured average diameter from the granulometrical analysis of agglomerates is 22 μm. The density of this sample is 2.115 g/cm^3.

According to different morphology and the specific surface area, a different reaction of these two samples during a thermal treatment could also be expected and that thermal treatment causes different changes to these samples as well.

In their original state, these two samples are amorphous (*Fig3*). To define the temperature intervals where the changes occur, DT and TG analysis are done and shown in *Figs. 4* (sample1) and *5* (sample 2). The first endothermic effect is double and shows loosing physically absorbed free water from mezopores and micropores, which are the main bearers of the absorption capacity. The second endothermic effect refers to loosing hydroxyl group.
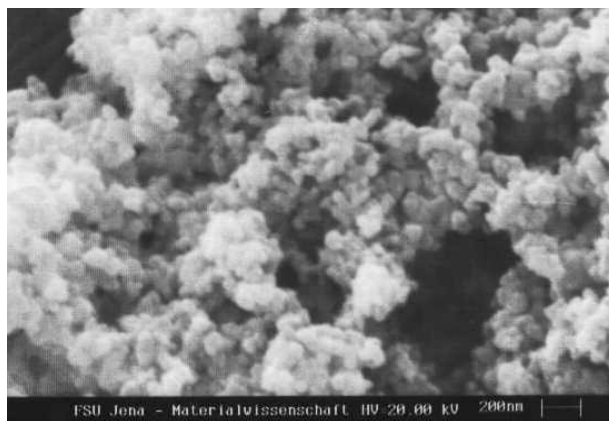

Fig. 1. SEM image of SiO$_2$ sample (obtained at ph $= 1$ and at 95 °C)

This occurs in a longer temperature interval. The first exothermal effect is a consequence of the morphological order of aggregates and agglomerates, and the second effect shows the transition to crystal state (crystobalite).

The explanation that follows refers to comparison between the two above mentioned effects for both samples (obtained at 80 and 95°C).

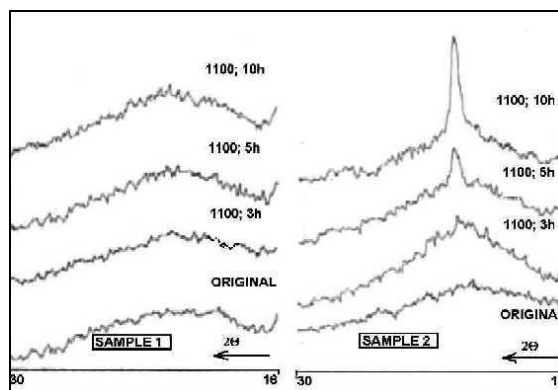Fig. 2. SEM image of SiO$_2$ sample (obtained at ph $= 1$ and 80 °C)

Fig. 3. X-ray diffraction pattern of calcined SiO$_2$ powders (obtained at 80 °C-sample 1, and 95 °C-sample 2) under different temperature conditions

3.1. Adsorbed Free Water

The sample obtained at 80 °C (1) shows that there is a bigger absorbed quantity of free water under certain ambient conditions (9.90%). The sample obtained at 95°C (2), which has absorbed 7.47% water under the same conditions. The difference is a direct consequence of and is proportional to the difference of the specific surface area. It depends on the dimensions of primary particles, aggregates and agglomerates and is especially a consequence of precipitation temperature. The second maximum of the first double endothermic effect shows a late loosing of water from micropores.
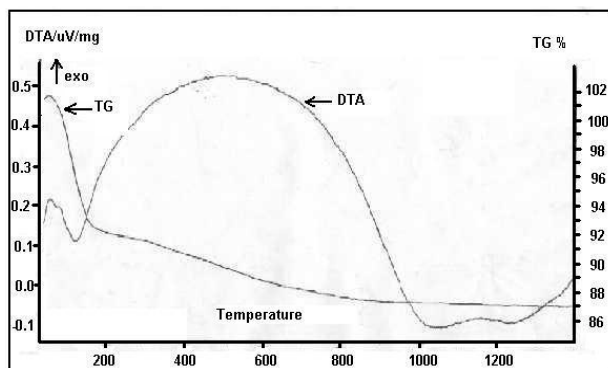
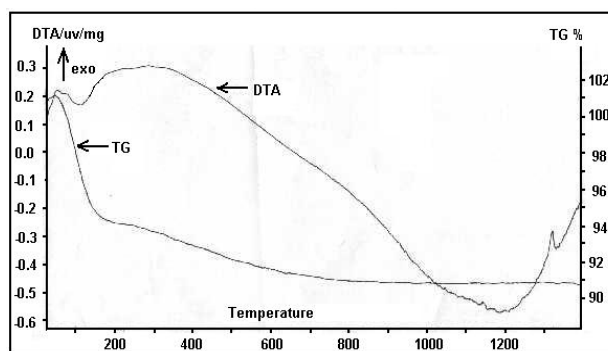*Fig. 4*. DT and TG analysis of sample 1 (obtained at 80 °C)

Fig. 5. DT and TG analysis of sample 2 (obtained at 95 °C)

3.2. *Morphological Changes*

Especially important change is the one that begins at the temperature interval $180 - 200$ °C, and completes at $500 - 550$ °C (for sample $2 - 95$ °C), and $900 - 950$ °C (for sample $1 - 80$ °C). In these temperature intervals the process of morphological consolidation (consolidation of the texture) of the agglomerates and especially of the aggregates occurs. As this material (amorphous precipitate SiO_2) is of fractal nature [3, 5] the empty space among the primary particles begins to disappear. The same happens with the empty space between aggregates of which the agglomerates consist. Consequently, the packing density, especially of the aggregates, increases. That blocking of the pores among them blocks the free surface of the primary particles. As a consequence of this process a drastic reduction of specific surface area occurs. The specific surface area of sample 1 is reduced from 465 to 285 m^2/g, and the specific surface area of sample 2 is reduced from 312 to 73 m^2/g (*Table 1*). It could be considered that the change of sample 2 (95 °C) is completed after a 10-

hour heating process at 530 °C. The same change for sample 1 (80 °C) continues up to approximately 950 °C (*Fig. 4*). The prolonged consolidation of sample 1 is a consequence of a higher number of contacts among the primary particles because of their smaller dimension and more particles in the same mass. The energy value of this morphological consolidation of sample 1 is 7222.34 J/g, and 8144.85 J/g of sample 2 (DSC analysis performed at Perkin-Elmer DSC7). Because these values are obtained at up to 530 °C, as the relevant could be considered the one of sample 2 (where the process is completed (*Fig. 5*)), while the energy value of sample 1 is actually twice as big as that of sample 2. Following this, the temperature of 530°C allows the process of consolidation for sample 1, only up to the half of the whole possible reaction (*Fig. 4*). The faster final consolidation of the sample obtained at 95 °C and the less energy value of the process shows existing of a state which is closer to a structural order, comparing to the sample obtained at 80 °C. Both samples stay still amorphous, and their RTG analyses are identical to those from their original (green) state.

Table 1. Specific surface area of SiO_2 samples treated under different temperature conditions

Sample	Specific surface area (m^2/g)			
	Original	530 °C; 10h	1100 °C; 5h	1100 °C; 10h
1.	465	285	66	24
2.	312	73	57	0.0383

3.3. Crystallization

The last significant change to sample 2 occurs at 1315 °C while this change does not happen to sample 1 at all, below 1400 °C. To show a more obvious difference between both samples, they are heated at a lower temperature (1100°C) with prolonged time (1; 3; 5 and 10 hours). Because of the higher energy acceptability, and higher density of the sample obtained at 95 °C, it begins to transform into the cubic crystal structure of crystobalite. The sample obtained at 80°C still remains amorphous (there is a probability that it is in a cryptocrystal state because of its enlarged exothermal peak in the interval of $1150 - 1220$°C; it is possible that the same peak shows a secondary morphological consolidation, that is, consolidation of the aggregates in the agglomerates. At these temperatures the aggregates paste together too (besides the first pasting together of the primary particles), followed by disappearance of the pores at this level too, even besides a partial sintering of the biggest particles-agglomerates. As a consequence of these changes the specific surface area drastically reduces. This reduction increases with the heating time,

and that means: after 5 h (1100 °C) sample 1 has 66 m^2/g and sample 2 $-$57 m^2/g, while after 10 hours heating at the same temperature sample 1 has 24 m^2/g (*Figs. 6* and *8*) and sample 2 has only 0.0383 m^2/g (*Table 1*). The drastic reduction of the specific surface area of this sample is due to the transition of the material in a crystal state, and especially, the higher level of sintering of the primary particles, the aggregates and even the agglomerates. It is shown in the SEM micrograph (*Fig. 7*), and in the optical micrograph (*Fig. 9*), where pasting together even of the biggest particles is noticeable. (The optical micrographs in *Figs. 8* and *9* are made on 'Leitz – Orthoplan – Pol').
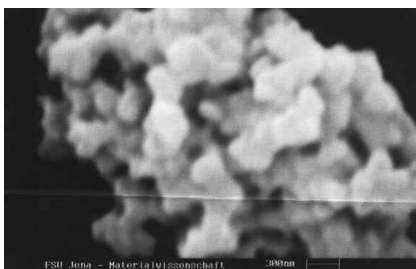

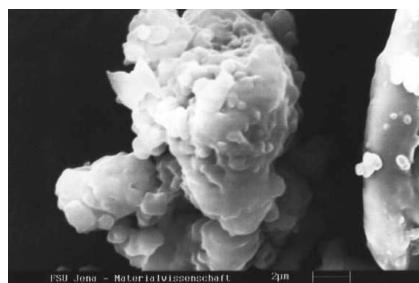*Fig. 6.* SEM image of sample 1 (1100 °C-10 h)

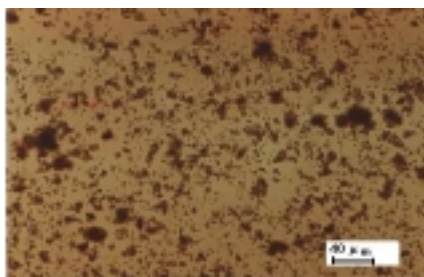*Fig. 7.* SEM image of sample 2 (1100 °C-10 h)

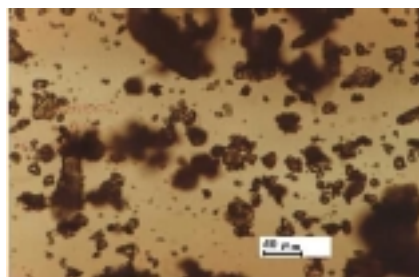*Fig. 8.* Optical micrograph of sample 1 (1100 °C-10 h)

Fig. 9. Optical micrograph of sample 2 (1100 °C-10 h)

4. Conclusion

The results from the experiments performed show the great influence of the precipitation temperature upon the structure and the properties of the samples obtained.

The mutual differences between the products are perceived by the following: The higher precipitation temperature (95 °C) causes creating of amorphous precipitate with bigger primary particles, a smaller specific surface area, and a higher density comparing to the sample obtained at a lower temperature (80 °C). The above mentioned differences enable faster and easier consolidation of the morphology (texture) of the particles and also the molecular structure, when the material is heated at the characteristic temperatures where the changes occur. On the opposite, the lower precipitation temperature, which is chosen to create a gel state instead of creating solid state particles (less primary particles, bigger specific surface area and lower density) enables creating of a more chaotic structure which is harder to bring in order (consolidate crystal structure) by heating. All this means a higher thermal stability too.

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