PARTICLES SiO₂ BY TETRAETHOXYSILANE HYDROLYSIS IN THE Si-O-H-C-N SYSTEM

I. Kayun, O. Musov. Thermodynamic of obtaining of monodisperse particles SiO₂ by tetraethoxysilane hydrolysis in the Si-O-H-C-N system. The problem of synthesizing mono dispersed SiO₂ particles with hydrolysis (C₅H₄O₃)Si by the Stober method is described. The purpose of the study is to determine the conditions for the passage of this reaction in a water-ammonia-alcohol medium, at which the maximum concentration of the solid phase of SiO₂ and the minimum concentration of silicon ion compounds in solution are reached. By thermodynamic modeling the composition of the Si-O-H-C-N system under thermodynamic equilibrium for various given conditions was studied. The maximum amount of solid phase SiO₂ at different initial concentrations (C₅H₄O₃)Si is achieved at an initial concentration of C₅H₄OH more than 1.2 mol/l, the concentration of the solid phase of SiO₂ is proportional to the initial concentration (C₅H₄O₃)Si. Thermodynamic studies show that a change in the reaction temperature from 1 to 70 °C does not affect the concentration of ionic silicon compounds in the solution and the solid phase of SiO₂. The obtained results reduce the search for optimal conditions for the production of monodisperse particles of SiO₂ and allow a deeper understanding of the processes taking place in the Si-O-H-C-N system.

Keywords: thermodynamics, Stober method, hydrolysis of tetraethoxysilane

Introduction. Actuality obtaining of mono-dispersed particles of SiO₂ due to their wide use in industry. This is the production of opals, photonic crystals, in the chemical industry as composite catalysts, etc.

Hydrolysis of tetraethoxysilane (TEOS) by the Stober method in a water-alcohol-ammonia medium allows for the obtaining of nano and submicron spherical particles of SiO₂ [1]. The size of SiO₂ particles synthesized by hydrolysis of TEOS largely depends on the concentration of TEOS, water, alcohol, ammonia and reaction temperature [2].

Due to the many components of the Si-O-H-C-N system, the development of technology for the synthesis of mono disperses spherical particles of SiO₂ requires numerous experiments. Thermodynamic studies will reduce their number, determine the conditions for which the maximum solid phase of SiO₂ will be obtained and determine the composition of the Si-O-H-C-N system, which greatly affects the characteristics of the synthesized particles [3].

Analysis of recent research and publications. The influence of water, ammonia and TEOS concentrations on the particle diameter and their uniformity in size was considered repeatedly [4]. The possibility to obtain homogeneous particle sizes at high concentrations of TEOS [5] was investigated.
The described work only partially investigated the problem of synthesis of monodisperse particles SiO$_2$. Restrict the search area of optimal conditions for the production of mono-dispersed SiO$_2$ particles is possible by thermodynamic studies. The thermodynamic study of tetraethoxysilane hydrolysis by the stoeber method has been given insufficient attention. There are studies that only partially describe the properties of the multi-component system Si-O-H-C-N. Calculated and experimentally confirmed data of thermo chemical parameters for 47 molecules in the Si-O-H system [6]. The thermo chemistry of compounds that can exist in the early stages of the high-temperature decomposition of TEOS in the preparation of amorphous silicon dioxide ($\alpha$-SiO$_2$) nano particles [7] is investigated.

Thus, the Si-O-H-C-N system, represented by tetraethoxysilane in a water-alcohol-ammonia environment, is not investigated from thermodynamic positions. However, there is information on the thermodynamic parameters of the compounds that make up the investigated system and can be formed as a result of the reaction.

The purpose of the study is to determine the conditions for the hydrophilic reaction of the TEOS in aqueous ammonia-alcoholic medium, in which the maximum concentration of SiO$_2$ solid phase and the minimum concentration of ionic compounds of silicon in the solution is reached.

Presentation of the main material. Synthesis of monodisperse particles of SiO$_2$ by hydrolysis of TEOS by the Stoeber method is carried out by reaction (1) in a water-alcohol-ammonia environment.

$$\text{Si(OSiH$_3$)$_4$} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH}. \quad (1)$$

The reaction components (1) form a system of Si-O-H-C-N, the thermodynamic studies of which are well described by a mathematical model created on the basis of the “Selector” software complex.

The principle embodied in the program is bishydrolysis of the component system, represented by tetraethoxysilane in a water-alcohol-ammonia environment, is not investigated from thermodynamic positions. However, there is information on the thermodynamic parameters of the compounds that make up the investigated system and can be formed as a result of the reaction.

The described thermodynamic model shows that the amount of solid phase SiO$_2$ depends on the concentration of C$_2$H$_5$ON. At the initial concentrations of H$_2$O=20 M, (C$_2$H$_5$O)$_2$Si=0.1 M, NH$_3$OH=1.5 M and at a temperature $T=25^\circ$C, the maximum solid phase of SiO$_2$ is formed at a concentration of C$_2$H$_5$CONH$_2$ greater than 0.9 M (Fig. 1). When the amount of alcohol from 0 M to 0.9 M changes, the concentration of H$_2$SiO$_4$ decreases with exponential dependence. A further increase in C$_2$H$_5$OH has little effect on their number. The concentrations of other compounds of silicon C are lower than those described above, so it is possible to assume that they will not affect the characteristics of the synthesized particles.

In order to obtain the maximum SiO$_2$ solid phase at different initial (C$_2$H$_5$O)$_2$Si concentrations, we established the required concentration of C$_2$H$_5$OH (Fig. 2), which can be determined by equation (2). Thus under conditions of thermodynamic equilibrium for any initial concentrations (C$_2$H$_5$O)$_2$Si the maximum amount of SiO$_2$ solid phase is reached at an initial concentration of C$_2$H$_5$OH of more than 1.2 mol/l.

$$y = 1.2 - 4*[\text{Si(C}_2\text{H}_5\text{O})_2] \quad (2)$$

In order to increase the SiO$_2$ solid phase, it is expedient to increase the initial number of TEOS. Fig. 3 shows the simulation results of the system Si-O-H-C-N at a temperature $T=25^\circ$C, which consisted of H$_2$O=20 M, C$_2$H$_5$OH=9 M, NH$_3$OH=1.5 M. As can be seen from Fig. 3 concentrations of SiO$_2$ and TEOS are proportional.
Concentrations of other compounds of silicon are practically unchanged. Simulation is limited by the maximum number of TEOS at which it is possible to obtain uniform spherical particles of size [3].

An increase in the initial concentration of NH₂OH from 0 to 1.9 M leads to a decrease in the SiO₂ solid phase in the SiO-H-C-N system at 1e⁻³ M at a TEOS concentration of 0.2 M (Fig. 4). Subsequent studies have shown that the indicated change in the solid phase SiO₂ concentration does not depend on the concentration of TEOS.

Fig. 1. Dependence of the concentration of silicon compounds (♦ - H₂SiO₄, ■ - H₂SiO₄⁺, ▲ - H₂SiO₄⁻, ● - HSiO₃, + - SiO₂*, ○ - SiO₂) from the initial concentration of C₂H₅OH at the thermodynamic equilibrium of the Si-O-H-C-N system

Fig. 2. The concentration of alcohol is required to obtain the maximum amount of SiO₂ solid phase at different initial concentrations Si(C₂H₅O)₄

Fig. 3. The dependence of the concentration of silicon compounds (♦ - H₂SiO₄, ■ - H₂SiO₄⁺, ▲ - H₂SiO₄⁻, ● - HSiO₃, + - SiO₂*, ○ - SiO₂) from the initial concentration of TEOS at the thermodynamic equilibrium of the Si-O-H-C-N system

Fig. 4. The dependence of the concentration of silicon compounds (♦ - H₂SiO₄, ■ - H₂SiO₄⁺, ▲ - H₂SiO₄⁻, ● - HSiO₃, + - SiO₂*, ○ - SiO₂) from the initial concentration of NH₂OH at the thermodynamic equilibrium of the Si-O-H-C-N system

It is known that for the complete passage of reaction (1), the minimum concentration of H₂O should be twice as high as the concentration of Si (OC₃H₇)₄. Given the experimental data, the indicated ratio should be greater [8].

Thermodynamic studies of the influence of the initial concentration of H₂O are shown in Fig. 5 (initial modeling conditions: NH₂OH=1 M, C₂H₅OH=9 M, (C₂H₅O)₄Si=0.2 M, T=25 °C) show that SiO₂ can be obtained at an initial concentration of H₂O equal to 0 M.

Since the model shows the thermodynamic equilibrium of the system Si-O-H-C-N, which is not limited in time, H₂O in the system is formed with NH₂OH and C₂H₅ON and it is sufficient for the complete passage of the reaction (1). Taking into account the kinetic constraints on obtaining SiO₂ particles, it is expedient to provide an initial ratio of H₂O/Si (OC₃H₇)₄>2 concentrations.

Investigated temperature range is due to boiling of the reaction mixture and its freezing is from 1 to 70 °C. Table 1 shows the simulation results of the system Si-O-H-C-N consisting of H₂O=20 M,
C₂H₅OH = 9 M, (C₂H₅O)₂Si = 0.2 M, NH₂OH = 1.5 M. Thus, under thermodynamic equilibrium conditions, the temperature change of the system is not affects the concentration of compounds of silicon in the solution and solid SiO₂ phase.

The results of the thermodynamic calculations show that SiO₂ solids in the Si-O-H-C-N system are formed at a wide variation of the reaction temperature and the concentrations of reagents (Table 2).

The ranges of variations of the parameters of the system S-O-H-C-N, in which a solid SiO₂ phase is formed

| Parameter | Concentration Si(OC₂H₅)₂ | Concentration H₂O | Concentration NH₂OH | Concentration C₂H₅OH | Temperature |
|-----------|---------------------------|-------------------|---------------------|----------------------|-------------|
| Value range | 0…1.2 M | 0…19 M | 0…1.9 M | 0…10 M | 1…70 ºC |

The experimental verification of theoretical studies was carried out at a temperature of T=25 ºC and the concentrations of reagents H₂O=20 M, C₂H₅OH=10 M, (C₂H₅O)₂Si=0.2 M. Experimental studies show that the practical yield of SiO₂ is less than the theoretical by 10…15 %, depending on the initial concentration of NH₂OH (Fig. 6).

In our opinion, the explanation for the difference in the results is the high concentration of NH₂OH (a weak base) in the solution at the completion of the reaction. And as a consequence, the pH value is 10.8 and above, which leads to a higher concentration of water-dissolved silicon ions compared to the theoretically calculated value. In thermodynamic calculations, the pH ranges from 6 to 7, which is explained by the partial conversion of NH₂OH into N₂ and NH₃ and their removal from the solution in the form of gas.

Conclusions Under conditions of thermodynamic equilibrium, obtaining the maximum solids SiO₂ at different initial concentrations (C₂H₅O)₂Si is achieved at an initial concentration of C₂H₅OH of more than 1 mol/l. The solid phase concentration of SiO₂ is proportional to the initial concentration of TEOS.

Thermodynamic studies show that SiO₂ can be obtained at an initial concentration of H₂O equal to 0 M. The increase in the initial concentration of NH₂OH from 0 to 1.9 M leads to a decrease in the SiO₂ solid phase in the SH-O-H-C-N system for 1e⁻³ M, regardless of the initial concentration of Table 1

Concentrations of compounds at the thermodynamic equilibrium of the Si-O-H-C-N system in the temperature range from 1 to 70 ºC

| Compound | H₂SiO₄⁺ | H₂SiO₄⁻ | H₂SiO₄^{2+} | HSiO₄⁻ | SiO₂⁺ | SiO₂⁻ |
|----------|---------|---------|-------------|--------|-------|-------|
| Concentration, mol/l | 2.85E–05 | 1.28E–13 | 3.24E–10 | 8.80E–09 | 1.35E–08 | 9.52E–06 | 2.00E–01 |

Fig. 5. Dependence of the concentration of silicon compounds (+ - H₂SiO₄⁺; - H₂SiO₄⁻; ● - HSiO₄⁻; ○ - SiO₂⁺; ▲ - SiO₂⁻) from the initial concentration of H₂O at the thermodynamic equilibrium of the Si-O-H-C-N system

Fig. 6. Comparison of thermodynamic calculations of SiO₂(Cₜ) initial concentration at initial concentration change of NH4OH (●) and experimentally obtained concentration (Cₑ) (●)}
TEOS. The change in reaction temperature from 1 to 70 °C does not affect the concentration of ionic silicon compounds in the solution and solid SiO₂ phase.

Due to the kinetic constraints of the hydrolysis reaction of the TEOS, the practical yield of SiO₂ is less than the theoretical by 10...15 %, depending on the initial concentrations of reagents.

Further study of the problem of obtaining mono-dispersed particles SiO₂ should be directed to the experimental study of the Si-O-H-C-N system in order to detect the influence of technological parameters on the shape, average size and dispersion of the sizes of synthesized particles.

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