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## ANALYSIS OF METHODS OF REGULATION OF SILICON DIOXIDE PARTICLES SIZE OBTAINED BY THE STOBER METHOD

Об'єктом дослідження є метод синтезу наночастинок діоксиду кремнію, а саме метод Штобера. Синтез частинок за допомогою Штобер-процесу є прикладом золь-гель методу – одного з найбільш практичних і регульованих способів отримання наночастинок регульованого розміру, форми і морфології. Метод Штобера є класичним підходом до синтезу наночастинок діоксиду кремнію, проте в існуючих роботах відсутній систематичний підхід до встановлення зв'язку між такими параметрами реакції, як концентрації компонентів, температура і час проведення процесу. В ході дослідження використовувалися різні види інформаційного пошуку і вивчення інформації. В результаті роботи отримано огляд, який здатний вирішити завдання систематизації впливу зазначених параметрів в умовах Штобер-процесу. Розглянуто способи регулювання розмірів частинок кремнезему, а саме зміна: температури в досить широкому діапазоні від 5 °C до 65 °C; концентрації TEOS/H<sub>2</sub>O/NH<sub>3</sub>; кількості і термодинамічної якості розчинника, а також вплив часу проведення реакції. Вплив зазначених параметрів розглядається не тільки з точки зору зміни окремого параметра, а й в комплексі з іншими. Встановлено закономірності зміни діаметра частинок для головних умов синтезу. Показано шляхи синтезу частинок методом Штобера від сотень нанометрів до мікрометрів. Показано, що для синтезу частинок з мінімальними розмірами необхідним буде зниження концентрації реагуючих компонентів: TEOS, H<sub>2</sub>O і NH<sub>3</sub>. Це дозволяє знизити швидкість процесів гідролізу і конденсації, а також розчинність проміжного [Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4-x</sub>(OH)<sub>x</sub>], що визначає відсутність перенасичення в процесі зародкоутворення. Визначальними факторами такого зниження є підвищена температура синтезу і використання більш полярних розчинників. Результати роботи можуть бути використані для управління синтезом наночастинок діоксиду кремнію для різних застосувань – від каталітичних систем до функціональних наповнювачів матеріалів і, зокрема, створення супергідрофобних структур.

**Ключові слова:** метод Штобера, наночастинок діоксиду кремнію, регулювання розміру наночастинок, золь-гель процес.

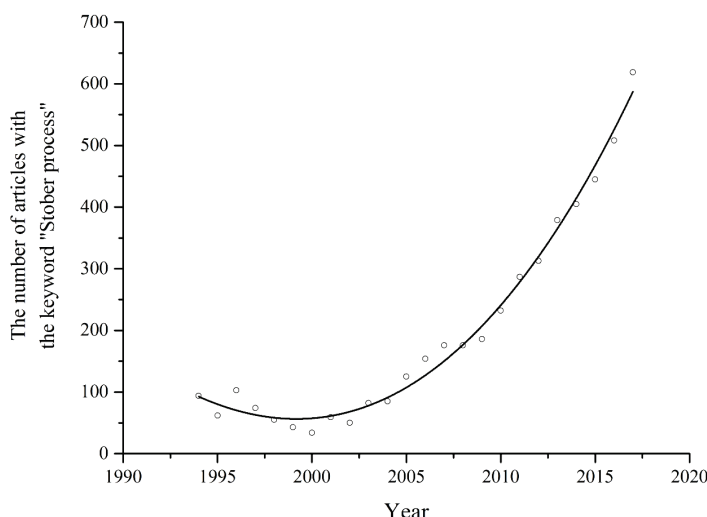
### 1. Introduction

Dynamic development of nanotechnology is observed in many fields of science. Particular attention is paid to the areas of technology, where current research is focused on the particle size, synthesis, surface characteristics and application.

Recently, the research community has shown great interest in nanostructures of nonmetallic oxides and their applications due to their simple synthesis procedure. In addition, these nanoparticles have a number of new properties, such as optical, magnetic, catalytic and mechanical.

One of the widely used oxides of nonmetals is silica nanoparticles [1, 2]. The quality of the products obtained depends strongly on the size and distribution of silica particles [3, 4]. Synthesis of silicon dioxide nanoparticles by the Stober method is the most rational. There are a number of parameters for the development of synthesis, changing which one can change the size of the nanoparticles obtained. In this connection, studies devoted to the systematization of parameters affecting the size of the final particles obtained in the synthesis of the Stober are relevant.

Interest in the study of nano-sized materials based on silica can be illustrated by analyzing the number of publications in the register [5] containing in the keywords the word «Stober process» from 1994 to 2017 (Fig. 1).



**Fig. 1.** Dynamics of interest in the research of the Stober process using the example of a search resource [5]

The data presented in the graph of Fig. 1 and the above information indicate an increase in interest in this subject, together with an increase in the practical significance of the results of synthesis of nanoparticles with controlled properties.

## 2. The object of research and its technological audit

*The object of this research* is control of the dimensions of the silica particles obtained during the sol-gel condensation within the process of the Stober process.

The influence of such factors as the concentration of active components in the classical Stober process, namely, tetraethoxysilane, water, and ammonia, is considered. In addition, attention is also paid to non-concentration factors, such as the temperature of the condensation process and the reaction time.

The need to select precisely these factors is caused by the absence of a systematic approach to regulating the particle sizes of silicon dioxide in existing works. In particular, most studies consider only certain factors, which limit the possibility of creating a general well-regulated model for obtaining the product of the desired granulometry. In turn, this narrows the possibilities of controlled synthesis of components, for example, for the production of functional fillers for composite materials, injection ceramics, systems with selective adsorption, and so on.

## 3. The aim and objectives of research

*The aim of research* is systematization and generalization of the methods for controlling the particle size of silica particles synthesized by the Stober method.

To achieve this aim, it is necessary to solve the following tasks:

1. To consider the basic conditions of synthesis by the Stober method and to determine the effect of these conditions on the particle size of the product of the process.
2. To formulate the main methods for regulating the particle size.

## 4. Research of existing solutions of the problem

There is an opinion that social and economic progress in the 21st century will be entirely determined by the successes of nanotechnology [6]. Modern science increasingly pays attention to nanomaterials and related technologies. In particular, over the last two decades, aspects of this branch of science have been studied, such as the production of nanostructures [7], the synthesis of nanoparticles [8] and films of nanometer thickness [9]. Nanoparticles are most often used as a source material for further modifications and the creation of structured ensembles. The production of monodisperse colloidal silica attracted considerable attention due to a wide range of potential applications, such as optical devices, magnetic particles, chromatography carriers, catalysts and additives to polymeric materials [1–3, 10, 11]. Their suitability for application in the form of photonic crystals [12, 13], chemical sensors [14], biosensors [15] is also extensively studied. In the early 2000s, there were many publications describing their use as nano-

filters for composite materials [16–18], sensors for controlled administration of drugs [19–22].

In the monograph [1], various methods for obtaining monodisperse silica are illustrated. A conventional method is the hydrolysis and condensation of tetraethylorthosilicate (TEOS) with water in the presence of ammonia as a catalyst [23]. Since the discovery on the basis of this reaction system, many studies have been carried out [24, 25]. In 1968, a systematic method for controlling the diameter of  $\text{SiO}_2$  particles in a range of sizes up to a micron was developed [26] and today this method is known as the Stober or SFB method. Subsequent publications describe the possibility of obtaining much smaller particle sizes of silicon dioxide [27–31].

During the research and changes in the Stober process, various formulations are described, particles with different diameters are obtained. The information already existing on this topic is quite extensive and needs to be generalized.

## 5. Methods of research

General scientific methods are used:

- method of analysis in studying the synthesis of silica particles by the Stober method;
- methods of systematization, classification and generalization when considering parameters that influence the course of the reaction flow, and subsequently on the size of the obtained silica particles.

## 6. Research results

The synthesis conditions, such as temperature, concentration and amount of reagents, as well as the type of solvent, directly determine the particle size of the silica. The use of these factors makes it possible to obtain silica particles in the range from 150 nm to 1000 nm. Next, the impact of each of these factors will be considered.

**6.1. Temperature.** For the temperature factor, the rule holds: the particle size decreases with increasing temperature (Fig. 2) [32–36].

It is established that the rate of nucleation increases with increasing temperature, the particle size decreases because of the high rate of nucleation [3, 37].

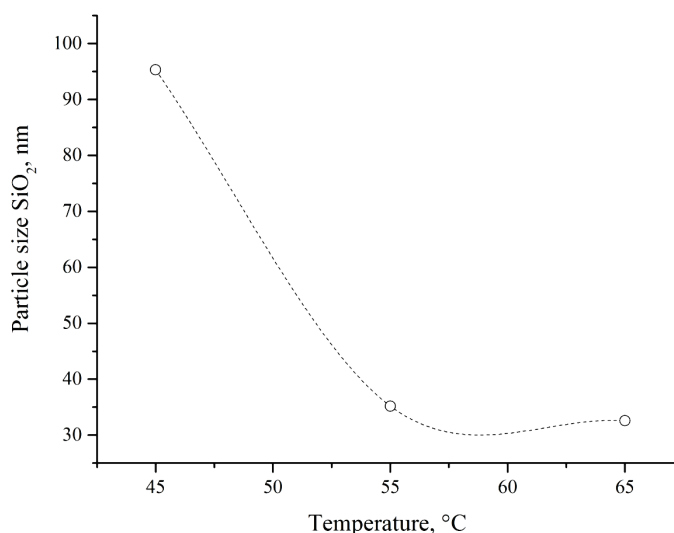
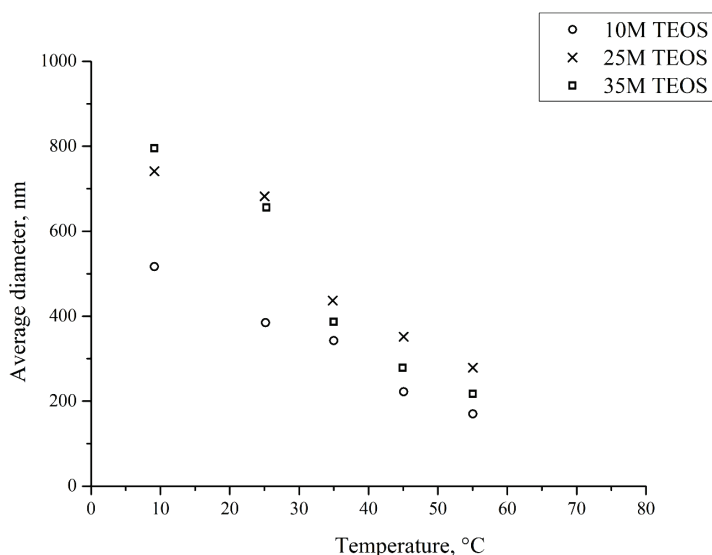


Fig. 2. Dependence of the particle size on the reaction temperature of the Stober reaction

From Fig. 2 that with an increase in temperature from 45 °C to 55 °C, the particle size decreased from 95 to 30 nm. However, with a further increase in temperature, no significant change is observed in the interval from 55 °C to 65 °C. With an increase in temperature to 65 °C, the particle size rises, which is explained by the authors of the study by the beginning of aggregation processes. They connect the process with increased solubility and an increase in the probability of collisions of particles at high temperatures [32].

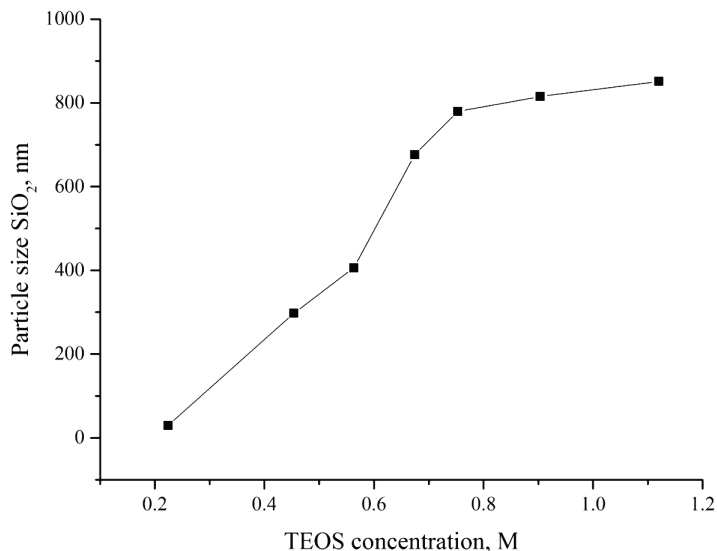
The publication [10] confirms that as the temperature rises, the particle size decreases. In the experiment it was shown that monodisperse particles in the range 920–940 nm can be obtained for a system with TEOS concentration of 1.24 M at a temperature of 5 °C, but for such reagent content at a temperature of 20 °C, aggregation intensification is likely. It follows that a decrease in temperature probably slows the hydrolysis and condensation of TEOS, and also reduces the frequency of thermal oscillations of oligomers. This can to some extent reduce the intensity of their aggregation, which leads to the formation of larger particles at a high concentration of TEOS. In [24] this assertion is clearly presented (Fig. 3).



**Fig. 3.** Dependence of the particle size on the reaction temperature of the Stober reaction at high TEOS concentrations

From Fig. 3 it follows that as the temperature rises under these conditions, the particle size decreases almost fourfold, from 800 to 200 nm. In general, the analysis of the dependencies presented in Fig. 2 and Fig. 3, indicates their similarity to different concentrations of TEOS. At the same time, it is obvious that the lower limit of the size is determined by the concentration of this reagent, and the very existence of this limit is the establishment of equilibrium between the mobility of oligomers and the stability of the system to aggregative and further coagulation changes.

**6.2. TEOS concentration.** TEOS particle size is directly related to the particle size of the product, which is confirmed by a number of experimental results [32, 33, 38–40]. For example, consider one of these dependencies (Fig. 4).



**Fig. 4.** Dependence of the particle size of silicon dioxide obtained by the Stober method on the TEOS concentration [10]

Since TEOS hydrolysis is the source of the monomer for subsequent condensation reactions, its concentration determines the concentration of nuclei/primary particles present in the system.

With an initial supersaturation of the solution, more embryos are formed which will induce the formation of more primary particles. Aggregation of primary particles leads to the formation of more stable secondary particles [24, 41]. After the induction period, any primary particles or nuclei that form will dissolve and re-precipitate on the growing secondary particles through the Ostwald ripening mechanism [42]. The process will continue until all primary particles are consumed or until a stable state is achieved [32]. So, when the TEOS concentration becomes larger, in the space between volumes during hydrolysis, the monomer produces more reaction intermediates, so larger particles can form when condensing these intermediates. In [24], a similar phenomenon is reported at 55 °C. The authors found that the particle size increased from 150 to 250 nm, when the TEOS molar concentration increased from 0.1 to 0.35 M.

The publication [32] shows that for a fixed concentration of ammonia ( $\text{NH}_3$ )=0.08 mol/l and water ( $\text{H}_2\text{O}$ )=0.04 mol/l, the particle size increases with increasing TEOS concentration to 0.80 mol/l and stabilizes at a value of about 90 nm.

This phenomenon confirms the increase in particle size due to an increase in the concentration of primary particles during the induction period. At a TEOS concentration of more than 0.80 mol/l ammonia is in short supply, which leads to the incompleteness of the hydrolysis and condensation reactions. As a result, the yield of the product falls by more than 50 % due to incomplete reactions, and the particle size remains almost constant (Fig. 5).

It is also like to note that with a strong supersaturation of the solution with TEOS, the expenditure of primary particles is much slower. Because of this, the primary particles are spontaneously aggregated to form stable secondary particles, which lead to a significant increase in the polydispersity of the particle size distribution (Fig. 6).

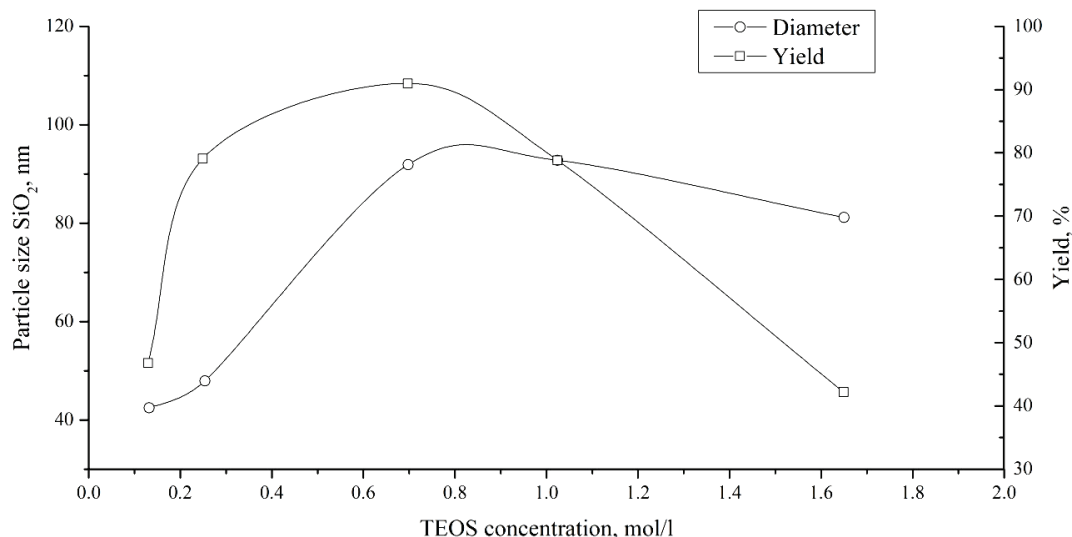


Fig. 5. Dependence of the size of the particles of the Stober process product on the TEOS content in the system according to the data of [32]

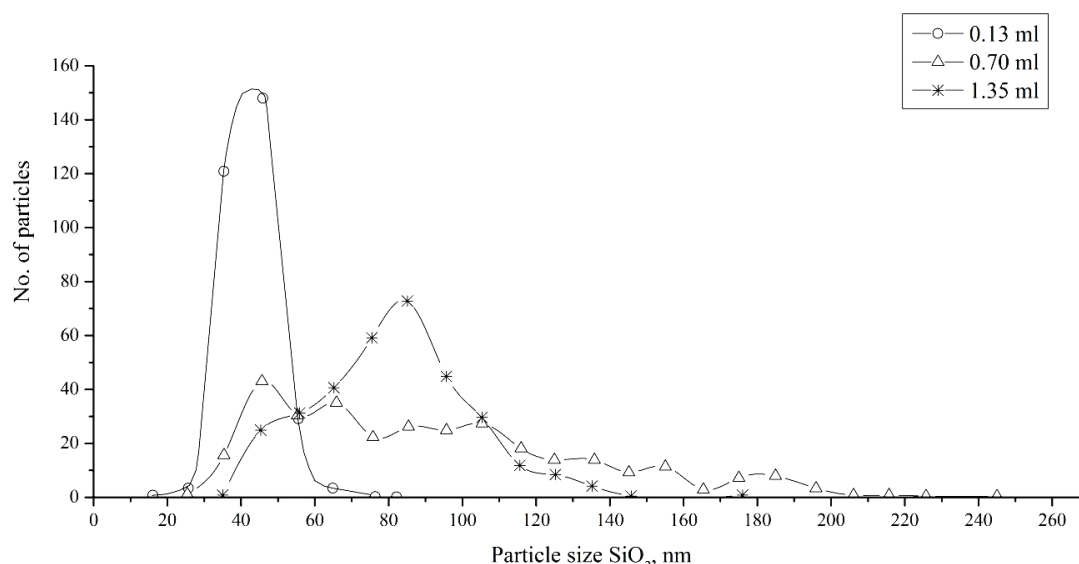


Fig. 6. The distribution of silica particles in size, depending on the TEOS concentration according to the data of [43]

**6.3. NH<sub>3</sub> concentration.** In the Stober process, ammonia is used as a pH regulator of the medium. In earlier works it was stated that the particle size increases with increasing NH<sub>3</sub> concentration [33, 44], which is shown in Fig. 7.

A graph for the TEOS concentration of 0.087 mol/l is given in [44]. In both solvents, an increase in the concentration of ammonia leads to an increase in the average particle size.

This effect is stronger in methanol. Particles grown in ethanol are larger than particles in methanol, and this is more pronounced in the concentration region with a low content of ammonia.

This difference gradually decreases as the pH regulator increases and, eventually, the particles in any solvent grow to comparable sizes. The presence of ammonia increases the rate of TEOS hydrolysis [27, 32, 42, 45, 46]. And it also increases the condensation rate of hydrolyzed monomers [42, 45, 46]. This leads to an increase in the particle size of the silica.

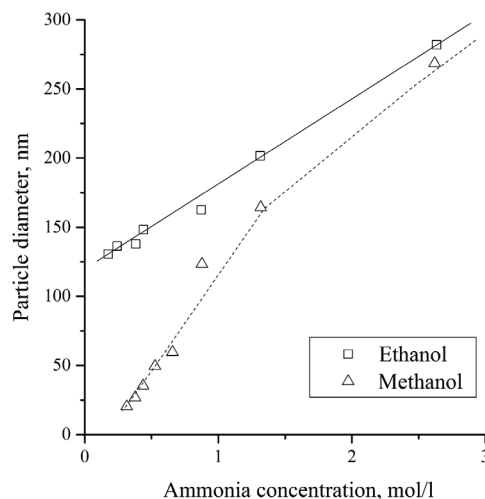
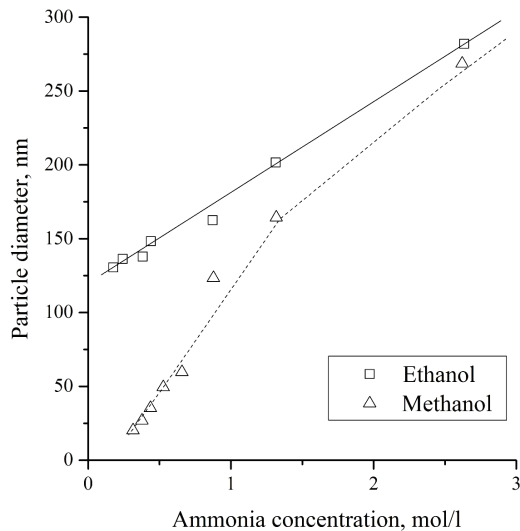


Fig. 7. The effect of ammonia concentration on the average particle size of the product according to [33]

The yield also increases to a maximum of 95 % with an increase in the  $\text{NH}_3$  concentration to 3.0 mol/l, indicating a near complete completion of the process. The particles obtained at higher concentrations of  $[\text{NH}_3]$  have a smooth surface, a spherical shape with no aggregation.

Beginning in 2010 [10, 40], the publications supplement information on the ammonia effect on the growth of silica particles in the process of the Stober.

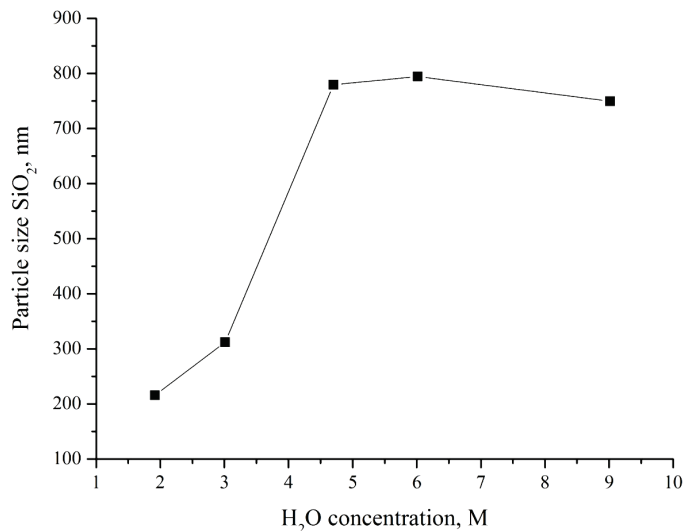
The dependence of the size on the  $\text{NH}_3$  concentration has an extreme character with a pronounced maximum (Fig. 8).



**Fig. 8.** The supplemented dependence of the particle size of silicon dioxide on the ammonia concentration according to the data of [10]

A sharp increase in the growth rate of particle sizes, shown in Fig. 7, can also be explained by the onset of aggregation, in this case at an ammonia concentration of 0.8 mol/l. The condition of aggregation is the ratio of hydrolysis and condensation rates: this happens if the condensation rate is greater than the TEOS hydrolysis rate.

**6.4.  $\text{H}_2\text{O}$  concentration.** As the amount of  $\text{H}_2\text{O}$  (M) increases, the particle size increases to a certain peak (Fig. 9), after which the particle size slowly decreases with a further increase in concentration [3, 10].

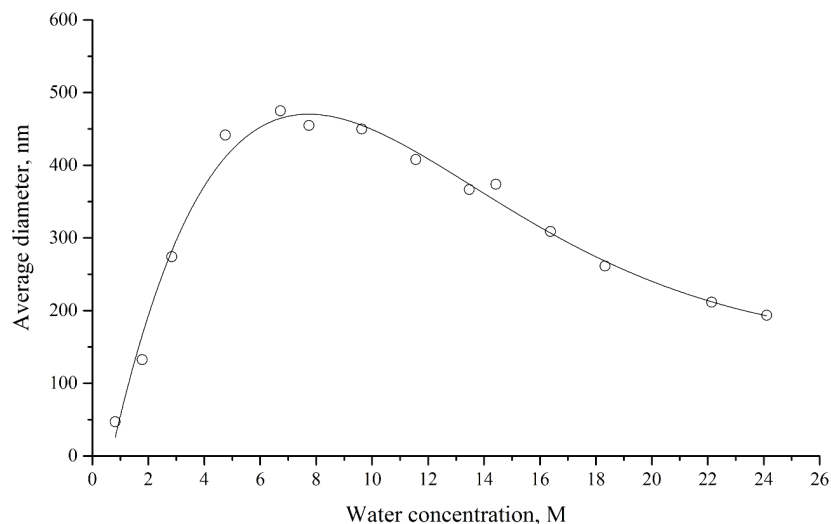


**Fig. 9.** The effect of water concentration on the average particle size in the Stober process according to the data of [10]

Fig. 9 shows that the effect of water concentration on particle size is similar to that of  $\text{NH}_3$  concentration. Namely: the particle size increases with increasing concentration of  $\text{H}_2\text{O}$  and reaches a maximum value, in this case – about 6 M, and then falls with increasing concentration. This result agrees well with the results of [24, 33, 47].  $\text{H}_2\text{O}$  can accelerate the TEOS hydrolysis, promoting the formation of larger particles, whereas at a higher concentration,  $\text{H}_2\text{O}$  dilutes the oligomers in the reaction solution, resulting in a smaller amount of particles.

Similar results are presented in [24] (Fig. 10).

The curve in Fig. 10 has a clearly pronounced maximum, but since other ratios of TEOS/ $\text{NH}_3$ , were used in the experiment [24], the average particle size of  $\text{SiO}_2$  differs from the data in Fig. 9.



**Fig. 10.** The effect of water concentration on the average particle size of silica obtained by the Stober method according to the data of [24]

**6.5. Quantity and polarity of solvent.** The dependence of the growth of the diameter of silica particles on the decrease of the volume of the solvent (ethanol) in the solution is demonstrated in [48] (Fig. 11).

In the publication [33], the Stober synthesis is carried out in a number of solvents of one homologous series with different values of the permittivity, such as methanol = 32.6; ethanol = 24.3; propanol = 20.1; butanol = 17.8. This determines the particle size in the process of nucleation by changing the balance between van der Waals forces of attraction and electrostatic repulsive forces. The latter increases with an increase in the dielectric constant of the medium, which ultimately leads to a decrease in the particle size [10, 49].

The question of the effect of the thermodynamic quality of the solvent on both the particle size of the product and the kinetics of the nucleation, condensation, and particle

stabilization processes is thus not sufficiently considered in the literature. In particular, the research in this direction could be promising in this direction from the point of view of the Flory theory or Hansen approach.

**6.6. The influence of the reaction time on the final particle size.** Initially, it is concluded in the studies that the optimum reaction time for the termination of the Stober process should be in the range of 3 to 12 h to achieve finite particle sizes [3, 20, 24, 50]. But in a later publication [48] this claim is refuted (Fig. 12).

Based on these data, it can be concluded that the processes are almost complete in about 2 hours of reaction. A sufficiently high degree of conversion (more than 90 %) is achieved in the first 30 minutes of the reaction. The reaction rate depends on the ethanol content of the system, it increases significantly with decreasing its concentration.

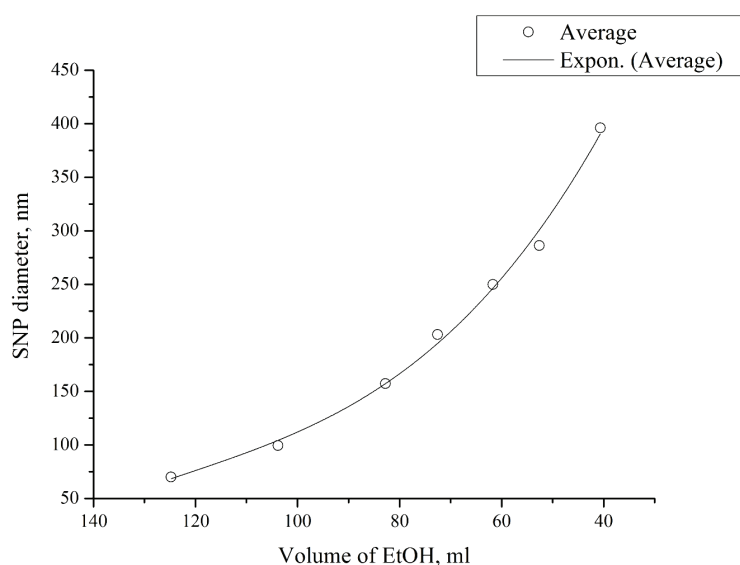


Fig. 11. Influence of the solvent content on the particle size of the Stober reaction product according to the data of [48]

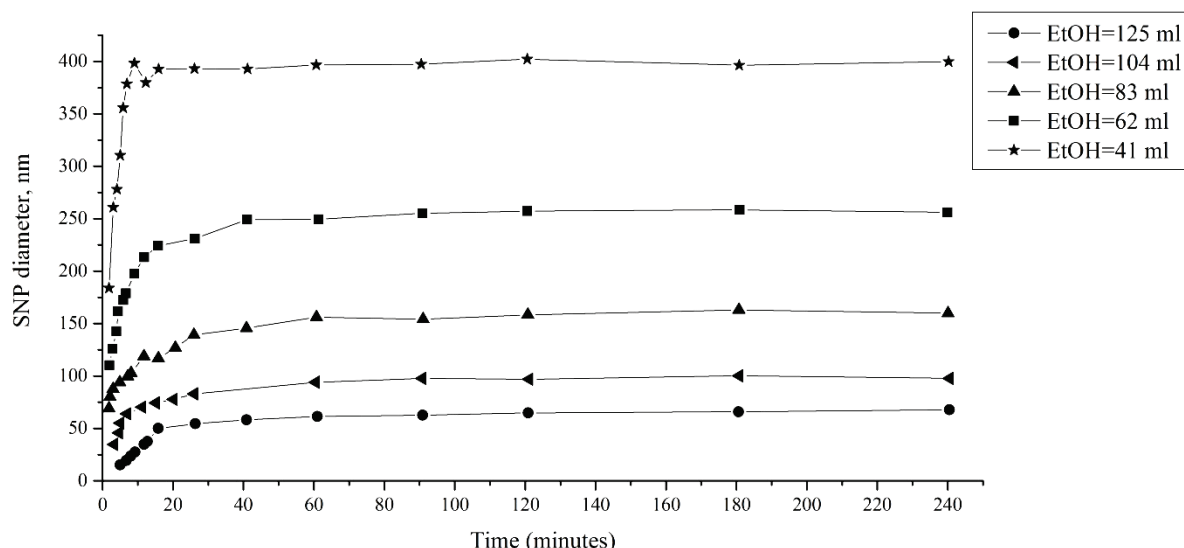


Fig. 12. The effect of the reaction time in the Stober process on the particle size of silica according to the data of [48]

## 7. SWOT analysis of research results

*Strengths.* Among the strengths of this research, it is necessary to note the systematization of methods for regulating the particle size of silica and the generalization of possible variations in the diameter of nanoparticles. The above results of the analysis of world scientific periodicals in which such full and broad description of the factors affecting the process are noteworthy in favor of this assertion. The use of the obtained data allows to solve the problem of choosing a rational regulatory factor or to use a complex approach to changing process parameters.

*Weaknesses.* The weak side of complex regulation of the parameters of nanoparticles obtained in the Stober process is the need for precise regulation of both component concentrations and temperature and reaction time factors. The solution to this problem is process automation, which is resource-intensive. Specific requirements for the purity of the starting materials also lead to an increase in the cost of raw materials.

*Opportunities.* When industrial synthesis of nanoparticles with controlled granulometry is set up using the Stober method, a number of markets are opened for the producer:

- 1) market of semi-finished products for the paint and varnish industry;
  - 2) market for additives to polymeric materials;
  - 3) market of semi-finished products of cast ceramics.
- To use the product in an industry, extensive research should be conducted on its effectiveness in these areas.

*Threats.* The main problem of the described technology is the lack of its profiling for this or that end product. It is the establishment of the effectiveness of the action of the additive in one or another case and the choice of adequate synthesis conditions and will be a source of additional costs.

At the moment, there is a technology for the synthesis of pyrogenic silica, aerosil, which is close to that described. The competitive advantages of this technology include lower energy costs and, consequently, a lower cost of the product.

The technology of synthesis by the Stober method, however, allows to obtain more controllable granulometry and smaller sizes of silica particles, as well as to increase the dispersibility of the obtained particles in different matrices.

## 8. Conclusions

1. The methods for regulating the particle sizes of silicon dioxide obtained in the course of the synthesis using the Stober method are systematized. The influence of changes in the concentrations of the main reagents of the process, as well as the temperature and duration of the reaction, is shown.

The character of the concentration dependences of tetraethoxysilane, ammonia and water has a clearly pronounced extreme character with a maximum for each individual reagent, which can be explained by the balance between hydrolysis, condensation and aggregation of the reaction product particles.

It is shown that temperature is also an important factor in controlling the particle size. The increase in temperature makes it possible to reduce this parameter to 4–5 times, which is explained by an increase in the thermal mobility of oligomers during condensation. At the same time, there is a certain temperature limit at which the system collides with the aggregative instability of the products formed.

The optimum reaction time is up to 2 hours, with the main processes of particle formation occurring within the first 30 minutes. It is shown that the change in the permittivity of the solvent can also serve as a tool for controlling the particle size of silicon dioxide. At the same time, in existing works there is no description of this method from the point of view of more modern theories dealing with the thermodynamic quality of a solvent, for example, Flory theory or Hansen more applied approach.

2. The main methods for controlling the particle size of silicon dioxide are formulated and described. Depending on the specified silica particle size, varying the above described parameters by the methods considered in the work, it is possible to synthesize particles ranging in size from hundreds of nanometers to micrometers. It is shown that in order to obtain particles with minimum dimensions it is necessary to reduce the concentration of reacting components: TEOS, H<sub>2</sub>O, NH<sub>3</sub>, increased synthesis temperature, and use of solvents with increased polarity.

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