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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Sol–Gel Synthesis of Monodispersed SiO_2 Nanoparticles in the Presence of Organic Amines

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Abstract—Preparation of monodispersed SiO_2 nanoparticles of varied size by hydrolysis of tetramethoxysilane and polycondensation of the hydrolysis products was studied as influenced by the basicity and nucleophilicity of organic amines.

In 1967, Stöber and Fink [1] showed that hydrolysis of silicon alkoxides in the presence of ammonia yields SiO_2 nanoparticles with narrow particle size distribution. Since that time, suspensions of particles of this kind became commercially available and found wide application in electronics and for preparing composites, monolithic glasses for optics, etc. [2, 3]. It is also known that hydrosols of these particles yield colloids with alternating structure (colloidal crystals), which are unique models for fundamental study of various types of interparticle interactions [4, 5] and crystallization from solution [6].

Although obvious progress has been achieved in the synthesis of SiO_2 nanoparticles, the results obtained are poorly reproducible [7]. To enhance the reproducibility, the effect of various factors on the size of SiO_2 nanoparticles was examined. In particular, the type of the initial alkoxysilane and alcohol used as the solvent, temperature of the sol–gel process, alkoxysilane concentration, alkoxysilane-to-water ratio, ammonia concentration, and rate of alkoxysilane addition were varied [1, 7–9]. However, there is one more factor affecting formation of a SiO_2 dispersion in the course of a sol–gel process: nature of the base catalyst, not examined in previous papers. Let us consider chemical reactions involved in this process [10]:

$$\equiv\text{Si–OR} + H_2O \underset{\text{Etherification}}{\overset{\text{Hydrolysis}}{\rightleftarrows}} \equiv\text{Si–OH} + \text{ROH}, \quad (1,2)$$

$$\equiv\text{Si–OR} + \text{HO–Si}\equiv \underset{\text{Alcoholysis}}{\overset{\text{Condensation}}{\rightleftarrows}} \equiv\text{Si–O–Si}\equiv + \text{ROH}, \quad (3,4)$$

$$\equiv\text{Si–OH} + \text{HO–Si}\equiv \underset{\text{Hydrolysis}}{\overset{\text{Condensation}}{\rightleftarrows}} \equiv\text{Si–O–Si}\equiv + H_2O. \quad (5,6)$$

Hydrolysis of silicon alkoxide yields silanols [reaction (1)] which can condense by reactions (3) and (5). When the sol–gel process is performed in an alkaline solution, reactions of alcoholysis (4) and hydrolysis (6), which are responsible for growth of SiO_2 particles with a definite size distribution, prevail. The rate of all of these reactions is acceptable only in the presence of catalysts. However, the mechanism of the base catalysis was reduced in the literature and, in particular, in a comprehensive monograph [11] to a bimolecular nucleophilic attack (S_N2–Si) of the hydroxide anion at the silicon atoms of alcoxysilane to give a five-coordinate intermediate which eliminates the alcohol molecule ROH (hydrolysis) or the RO^- anion (condensation). Thus, it is assumed that the sol–gel process involving hydrolysis of a silicon alkoxide and condensation of the hydrolysis products is controlled exclusively by the concentration of OH^- anions. Any organic base, in particular a nitrogen-containing compound, can be considered a proton acceptor. Its strength can be estimated from the pK_a of the conjugated acid:

$$:NR_3 + H_2O \rightleftarrows HN^+R_3 + OH^-. \quad (7)$$

However, the processes occurring in the sol–gel system incompletely fit in the logical path: (i) increase in the strength of the organic base, (ii) increase in the concentration of OH^- anions, and (iii) acceleration of the hydrolysis and condensation. For example, it is known that, although F^- is a weaker base than NH_3,

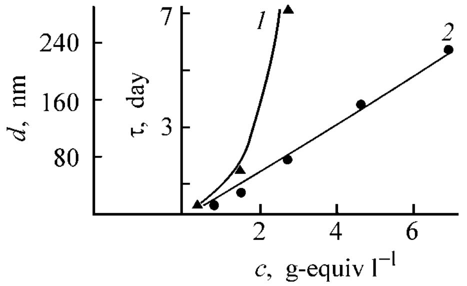


Fig. 1. (*1*) Average size d of SiO_2 particles and (*2*) gelation time τ vs. the 4-(dimethylamino)pyridine **V** concentration c in sol–gel systems 1–4 and 5b.

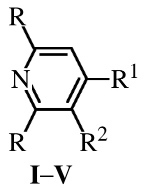
gelation of tetraethoxysilane solutions in the presence of KF is substantially faster than in the presence of the same amount of ammonia [11]. It is believed in this case that the F^- anion is close in size to the OH^- anion and can increase the coordination of the silicon atom in alkoxysilane [12]. In other words, not only proton affinity of the catalyst [Eq. (7)] but also its nucleophilicity (attack of its lone electron pair at the silicon atom of alkoxysilane) should be taken into account when describing the mechanism of the sol–gel process.

The nucleophilicity of a Lewis base depends on many factors, including the type of the chemical reaction involving this base [13]. In this study, we analyzed hydrolysis of tetramethoxysilane (TMOS) and polycondensation of the hydrolysis products in an alkaline solution in the presence of amines whose nucleophilicity was varied by changing the steric and electronic environment of the nitrogen atom.

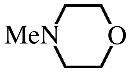
Thus, the present study was concerned with conditions for obtaining monodispersed SiO_2 nanoparticles and development of methods for preparative synthesis of this material.

EXPERIMENTAL

Base hydrolysis of TMOS and polycondenstaion of the hydrolysis products were studied in the presence of the following thermally and chemically stable organic amine cata lysts: pyridine (**I**), 4-methylpyridine (**II**), 3-ethyl-4-methylpyridine (**III**), 2,6-dimethylpyridine (**IV**), 4-(dimethylamino)pyridine (**V**), *N*-methylmorpholine (**VI**), piperidine (**VII**), *N*-methylpiperidine (**VIII**), and ethyldiisopropylamine (**IX**):

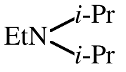


I–V



VI

VII, VIII



IX

Here R = R^1 = R^2 = H (**I**); R = R^2 = H, R^1 = Me (**II**); R = H, R^1 = Me, R^2 = Et (**III**); R = Me, R^1 = R^2 = H (**IV**); R = R^2 = H, R^1 = NMe_2 (**V**); R = H; (**VII**); R = Me (**VIII**).

TMOS and amines **I**–**IX** were distilled on a 10 TP column at atmospheric and reduced (15–760 mm Hg) pressure, with fractions boiling in the 0.5°C range collected. Amine **V** was recrystallized from alcohol. Sol–gel synthesis of SiO_2 nanoparticles was performed in a glass reactor equipped with a double water jacket, magnetic stirrer, dropping funnel, and reflux condenser. Appropriate amine, ethanol, and water were placed in the reactor. An ethanolic solution of TMOS (25 ml) was added with vigorous stirring at 70°C within 3 min. We prepared 13 sol–gel systems with TMOS : water : ethanol = 1 : 25 : 110. The mole fraction of amines is given below:

Sol–gel system	1	2	3	4	5a	5b	5c	5d	5e	6	7	8	9
Amine	**I**	**II**	**III**	**IV**	**V**	**V**	**V**	**V**	**V**	**VI**	**VII**	**VIII**	**IX**
Mole fraction	7.0	1.4	1.4	1.4	0.35	1.4	2.8	4.9	7.0	1.4	1.4	1.4	1.4

The particle size was determined with an EM-125 electron microscope at accelerating voltage of 75 kV. The samples were prepared by applying the suspension (in some cases, diluted by a factor of 2–3 with alcohol) to a carbon-reinforced collodion support.

The organic amines were chosen so that the acidity constants of their conjugated acids and their boiling points varied widely:

Amine	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	Ammonia
bp, °C [15]	115	145	198*	143–145		115–116**	124	106	127	
pK_a, 20°C [16]	5.20	6.02	6.46	6.77	9.70	7.38	11.3	10.20	10.50	9.25

All the experiments can be divided into three groups. In the first group, we varied the concentration of 4-(dimethylamino)pyridine **V** (sol–gel systems 5a–5d, Fig. 1). In the second, we varied the sub-

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* At 25°C [1, 5]. ** At 750 mm Hg.

stituients in the pyridine ring (sol–gel systems 1–4 and 5b). Electron micrographs of SiO_2 particles formed in these systems are shown in Fig. 2. In experiments of the third group, we used strong organic bases **V**–**IX**.

Prior to discussing the results obtained, the following should be noted. First, the resolution of the microscope used does not allow determination of particles smaller than 10 nm in diameter. Second, separate SiO_2 nanoparticles can be obtained only when TMOS is strongly diluted with ethanol and water, which promotes hydrolysis and alcoholysis of the Si–O–Si bonds in the sol–gel systems [Eqs. (4), (7)] [17]. Otherwise gelation of the sol is complete in less than 10 min in the presence of pyridine catalyst and is almost instantaneous in the presence of bases **V**–**VIII**.

The size of silica particles prepared by hydrolysis of TMOS and polycondensation of the hydrolysis products in the presence of 4-(dimethylamino)pyridine grows linearly with increasing amine concentration (Fig. 1). At amine concentration of 0.35 g-equiv l^{-1}, the particle size is close to the detection limit, whereas at amine concentration of 7 g-equiv l^{-1}, it is 210–240 nm. Since particles formed in alkaline solution are negatively charged and repel one another [18], they grow by the condensation mechanism through dissolution of smaller particles. These smaller particles are not perfectly spherical, with pointed projections and irregularities (Fig. 2b). It is these projections and irregularities that have an excess energy and initiate, in the first place, rupture of the Si–O–Si bonds. Hence, as silica particles grow, their shape becomes more spherical (Figs. 2c, 2d).

It should be noted that the dissolution and condensation to form an ensemble of spherical particles compete with polymerization gelation. Each of these processes prevails at a definite base concentration. Heating of sol–gel system 5b for 30 min does not cause particle coarsening but accelerates the gelation. Thus, at low catalyst content, small silica particles susceptible to polycondensation with inclusion of a solvent and to gelation are formed owing to insufficiently fast rupture–formation of Si–O–Si bonds. At high catalyst content (Fig. 2e, 7 g-equiv l^{-1}), large particles are formed. In this case, the sol degrades by sedimentation and subsequent coagulation. Sols prepared at a catalyst content of about 0.5 g-equiv l^{-1} are stable for many days (Figs. 2d, 2d).

It should be noted that all the above processes of silica nanoparticle formation in sol–gel systems 5a–5e are fast. Electron micrographs taken immediately after the reaction completion, i.e., several minutes after the onset of hydrolysis of TMOS and polycondensation of the hydrolysis products, are shown in Figs. 2a–2e. Such a high rate is provided by high basicity and nucleophilicity of 4-(dimethylamino)pyridine. When amines **I**–**IV** having a similar structure and lower basicity are used as catalysts, all these processes are strongly decelerated. Hardly visible particles are formed on heating at 70°C for 4 h in the presence of 4-methylpyridine (Fig. 2g). Silica particles generated in the presence of 3-ethyl-4-methylpyridine **III** within the same time are slightly larger. When the least basic amine, pyridine, was used, visible particles (Fig. 2f) were formed only after keeping the sol–gel system at 70°C for 8 h and then at room temperature for 8 days. The behavior of sol–gel systems 1–3 correlates with an increase in the amine basicity. However, no visible particles appear when sol–gel system 4 containing 2,6-dimethylpyridine is heated for 4 h, although the basicity of this amine is substantially higher than that of amines **I**–**III**.

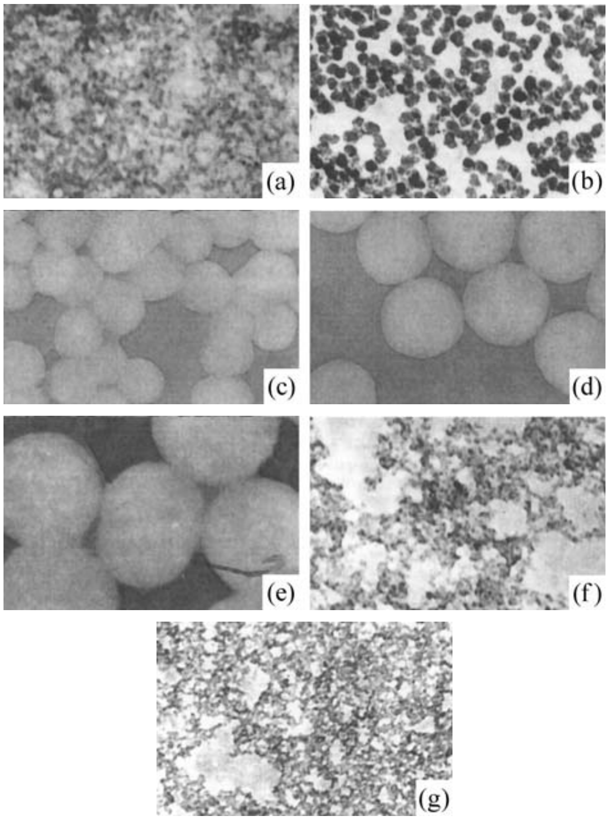

Fig. 2. Electron micrograhs of SiO_2 particles prepared in sol–gel systems (a) 5a, (b) 5b, (c) 5c, (d) 5d, (e) 5e, (f) 1 and (g) 2. Magnification ×100 000 (100 nm in 1 cm); the same for Fig. 3.

Thus, the mechanism of formation of silica nanoparticles in the presence of organic amines must involve an attack on the silicon atoms by the lone elec-

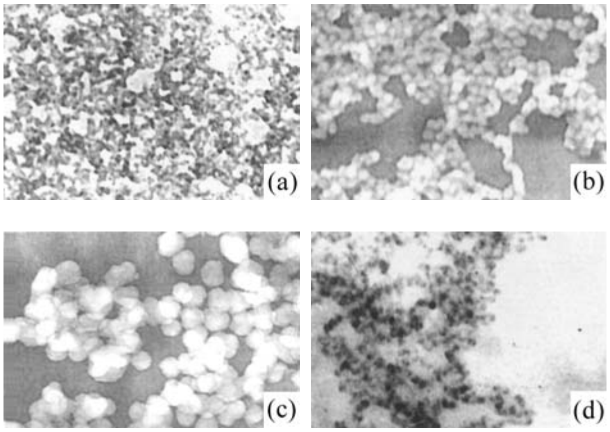

Fig. 3. Electron micrographs of silica particles formed in sol–gel systems (a) 6, (b) 8, (c) 7, and (d) 9.

tron pare of the nitrogen atom. If the electron pair is less accessible, as in, e.g., amine **IV**, owing to steric hindrance caused by two methyl groups, the sol–gel process is decelerated, i.e., it is controlled by the nucleophilicity, rather than basicity of the catalyst.

Clearly, this assumption is true when strongly basic amines **V**–**IX** are used as catalysts. Electron micrographs of SiO_2 particles prepared by the sol–gel process catalyzed with these amines are shown in Fig. 3. Hardly visible silica particles about 10 nm in diameter are formed in the presence of *N*-methylmorpholine (Fig. 3a). The diameter of silica particles grows with increasing amine basicity in the order *N*-methylmorpholine **VI** < 4-(dimethylamino)pyridine **V** (Fig. 2b) ~ *N*-methylpiperidine **VIII** (Fig. 3b) << piperidine **VII** (Fig. 3c). However, when less nucleophilic sterically hindered ethyldiisopropylamine is used, the particle size sharply decreases despite the high basicity of the amine (Fig. 3d).

CONCLUSIONS

(1) The procedure developed for preparative synthesis of monodispersed SiO_2 nanoparticles gives well-reproducible results and requires simple equipment.

(2) When a strongly basic amine ($pK_a > 9$) is used as catalyst, the particle size grows almost linearly with its increasing concentration.

(3) Catalytic hydrolysis of TMOS and polycondensation of the hydrolysis products to form SiO_2 nanoparticles are governed not only by the concentration of hydroxide anions in a solution (i.e., by basicity of an amine), but also by the nucleophilicity of the amine.

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