INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Sol–Gel Synthesis of Dispersed ZrO₂ Nanoparticles

N. N. Khimich, O. V. Semashko, E. N. Khimich, and M. G. Voronkov

Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia St. Petersburg State University, St. Petersburg, Russia

Received December 27, 2005

Abstract—The influence exerted by the basicity of organic amines on hydrolytic polycondensation of zirconium tetraisopropoxide was studied in order to obtain nanodispersed ZrO₂ particles of various sizes.

DOI: 10.1134/S1070427206030025

Hydrolysis of tetraalkoxysilianes, leading to formation of SiO₂ nanoparticles with a narrow size distribution, has been studied in sufficient detail [1-5]. The influence exerted by the structure of the starting alkoxvsilane and an alcohol used as a solvent, concentrations of the alkoxysilane and water, temperature of the sol-gel process, rate of addition of the alkoxysilane, and acidity of the medium has been examined [1-4]. As a result, suspensions of monodisperse SiO₂ particles have become commercially available and found wide use for synthesis of monolithic optical glasses and nanocomposite materials, in optoelectronics, etc. [6, 7]. Hydrosols of particles of this kind form periodic colloid structures, which are unique model systems for fundamental studies of interparticle interaction forces of varied nature [8, 9].

In contrast to the case of tetraalkoxysilanes, the formation of hydrosols of zirconium dioxide in hydrolytic condensation of its alkoxides has been studied to a considerably lesser extent. Let us consider chemical reactions (1)–(6) occurring in this process [10]:

$$\operatorname{Zr}(\operatorname{OR})_4 + n\operatorname{H}_2\operatorname{O} \xrightarrow{\operatorname{Hydrolysis}(1)}_{\xleftarrow{}} \operatorname{Zr}(\operatorname{OH})_n(\operatorname{OR})_{4-n} + n\operatorname{ROH}_4$$

$$\equiv Zr - OR + HO - Zr \equiv \frac{Condensation (3)}{(Alcoholysis (4))} \equiv Zr - O - Zr \equiv + ROH,$$

$$\equiv Zr-OH + HO-Zr \equiv \xrightarrow[Hydrolysis (6)]{Condensation (5)} \equiv Zr-O-Zr \equiv + H_2O$$

Despite the apparent similarity of hydrolysis of Si and Zr alkoxides [reaction (1)] and of polycondensation of the forming compounds [reactions (3) and (5)], the formation of ZrO₂ nanoparticles has its distinctive features. This is due, on the one hand, to the tendency for zirconium atoms to increase their coordination number to eight and, on the other, to the markedly higher basicity of the oxygen atom in the \equiv Zr–OH group, compared to that in =Si-OH (electronegativities of Zr and Si atoms by Pauling are equal to 1.2 and 1.8, respectively). Therefore, zirconium alkoxides have oligomeric structure in contrast to silicon alkoxides, which are monomeric. Zirconium alkoxides contain, as shown in detail for the example of zirconium tetraisopropoxide (ZTIP), alkoxy and oxo fragments in various combinations, with the relative amounts of these fragments dependent both on the preparation technique and on the storage duration of the samples synthesized [11, 12].

Owing to the increased basicity of the oxygen atom in the \equiv Zr–OH group, compared to the \equiv Si–OH group, the former is more labile in hydrolysis. As a result, the equilibrium of reactions (1) and (2) for zirconium alkoxides is strongly shifted to the right. The condensation reactions (3) and (5) are accompanied by formation of structures that contain a large number of hydroxy groups, which is quite untypical of silicon compounds. The reactions of alcoholysis (4) and hydrolysis (6) of these condensation products, which are responsible for the size ordering of oxide particles and for their growth, occur in the case of zirconium compounds by more complex mechanisms, compared to silicon compounds.

Until now, ZrO_2 hydrosols have been synthesized and the corresponding synthesis mechanisms have been studied in a weakly acidic medium [13–15]. Presumably, the forming suspensions of particles more than 1 µm in size [14] are poorly stable. It may be assumed that the sol-gel method for synthesis of monodisperse ZrO_2 particles of various sizes by hydrolysis of zirconium tetrabutoxide [15] is seemingly preferable. However, the too complicated experimental procedure and the limited amount of water used for hydrolysis of zirconium tetrabutoxide cast doubt on the completeness of hydrolysis, i.e., on the purity of the oxide synthesized.

The influence exerted by the basicity and nucleophilicity of a number of organic amines on the hydrolysis of tetramethoxysilane (TMOS) and on the polycondensation of the compounds being formed has been studied previously in order to obtain monodisperse SiO₂ particles of prescribed size [5]. The simplicity of this process and of the apparatus involved, as well as the good reproducibility of the results obtained, stimulated studies of the hydrolytic polycondensation of zirconium alkoxides under similar conditions. It was intended to study fundamental aspects of formation of monodisperse ZrO_2 nanoparticles under similar conditions and to develop optimal conditions of their synthesis.

EXPERIMENTAL

The hydrolysis of ZTIP and the polycondensation of the forming compounds were studied under conditions of base catalysis. As catalysts served amines: pyridine (I), 4-(dimethylamino)pyridine (II), and ethyldiisopropylamine (III); as well as tetra-*n*-butyl-ammonium hydroxide (IV) $(n-Bu)_4N^+OH^-$:



where R = H (I) and NMe₂ (II).

Zirconium tetraisopropxide was synthesized using the previously described method [16, 17] and purified by triple recrystallization from isopropanol. Amines **I** and **III**, preliminarily dried over BaO, were purified by distillation on a 10-TP column; they boiled within 0.2°C range. Amine **II** was recrystallized from ethanol. Hydroxide **IV** (Aldrich) was used without additional purification.

The sol-gel synthesis of ZrO_2 nanoparticles was performed in a glass reactor equipped with a double jacket for introduction of thermostating water, a magnetic stirrer, a dropping funnel, and a reflux condenser. The reactor was charged with ethanol, water, and an amine, and an isopropanol solution of ZTIP was added at 70°C under vigorous stirring in the course of 1 min. The total volume of the solution added was about 20 ml. A total of 12 sol-gel systems were prepared. The molar ratio alkoxide: water: ethanol: amine was 1:50:200:X, with the X values listed below:

Sol-gel system	Amine	X
1a	Ι	1.0
1b	Ι	5.0
1c	Ι	10
1d	Ι	20
1e	Ι	40
2a	II	1
2b	II	2
2c	II	3
2d	II	4
3	III	1
4	IV	1

The particle size in the sol-gel systems obtained was determined with an EM-125 electron microscope at an accelerating voltage of 75 kV. The samples studied were prepared by applying the suspensions obtained onto a carbon-reinforced collodion film substrate.

The choice of compounds **I**–**IV** is due to their different basicities, as characterized by the ionization constants of conjugated acids, pK_a :

$$:NR_3 + H_2O \rightleftharpoons HN^+R^- + OH^-.$$
 (7)

At 20°C, the pK_a values of the compounds used are as follows [18]:

 Amine
 I
 II
 III
 IV

 pK_a 5.20
 9.70
 10.50
 15.4

All the experiments performed can be conventionally divided into three groups. To the first of these belong experiments involving hydrolytic polycondensation of ZTIP in the presence of a nucleophilic base of medium strength, 4-(dimethylamino)pyridine (II) (sol-gel systems 2a-2e). The second group includes experiments with varied concentration of a weak base, pyridine (I) (sol-gel systems 1a-1e). Finally, to the third group belong experiments associated with hydrolysis of ZTIP in the presence of strong organic bases III and IV.

Figure 1 shows electron micrographs of particles in sol-gel systems 2a, 2c, and 2e. As the concentration of a base in the system increases, the forming ZrO_2 particles become coarser. However, the mechanism of their growth is apparently different from that in formation of SiO₂ particles in hydrolytic polycondensation of TMOS. In the latter case, the coarsening of



Fig. 1. Electron micrographs of particles in sol-gel systems (a) 2a, (b) 2b, (c) 2c, and (d) 3. Magnification 80000 (125 nm in 1 cm); the same for Figs. 2 and 3.

SiO₂ particles is accompanied by rupture of Si–O–Si bonds at places with an excess surface energy, specifically, at sharp projections and irregularities of the originally formed particles, which results in that they acquire a regular spherical shape [5]. According to Fig. 1, the coarsening of ZrO₂ particles is accompanied by aggregation of particles into a kind of clusters, rather than by growth of each separate particle. This involves sedimentation of the aggregated particles and the subsequent coagulation. As a result, loose nontransparent sediments are formed, with the rate of their formation being proportional to the concentration of the base. On passing from sol-gel system 2a to system 2e, the lifetime of the sol decreases from 10 days to several minutes. The difference between the processes of hydrolytic polycondensation of silicon and zirconium alkoxides can be understood as follows. According to Iler [19], silanols formed in hydrolysis of silicon alkoxides [reaction (1)] enter into condensation reactions (3) and (4). Successive elimination of water or alcohol molecules gives siloxanes of linear, cyclic, or polycyclic structure. After the polymerization is complete, particle of the dispersed phase of SiO₂ are formed and grow in solution. In the process, coarser particles grow by the condensation mechanism via dissolution of fine particles, with

virtually only siloxane bonds formed within coarsening particles and silanol groups predominantly situated on the surface of the particles. Such particles with a hydroxylated surface show mutual repulsion and, therefore, cannot aggregate and grow via condensation with molecules of the Si(OH)₄ monomer or siloxane oligomers from a true solution [19]. In the case of hydrolytic polycondensation of zirconium alkoxides, the pattern is different. First, formation of linear or cyclic polyzirconoxane bonds $-(Zr-O)_{\overline{n}}$ is not characteristic of zirconium. Second, oxygen compounds of zirconium are never present in hydroxyl-containing solvents in the form of monomeric or low-molecularweight oligometric species of the type $[Zr(OH)_4]_n$. Despite that the hydrolysis of the \equiv Zr–OR bond is considerably faster than the similar reaction for silicon, the ZrO_2 network



RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 79 No. 3 2006



Fig. 2. Electron micrographs of particles in sol-gel systems (a) 1a and (b) 1d.



Fig. 3. Electron micrographs of particles in sol-gel system 4 (a) before and (b) after gelation.

does not commonly appear in pure form (in contrast to the case of the siloxane bond). In all cases, polycharged aqua structures, e.g., species of the type $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ [20], are formed in the course of polymerization. Because of the large number of water molecules in the coordination sphere of a zirconium atom, the content of hydroxy groups on the surface of growing particles is insignificant, which allows their successful aggregation to give jelly-like sediments of hydrated ZrO_2 .

The course of the hydrolytic polycondensation of ZTIP is, undoubtedly, strongly affected by the pronounced nucleophilicity of the amine used (amine II). In hydrolytic polycondensation of ZTIP in the presence of base III, which has low nucleophilicity for steric reasons, but is considerably stronger, the degree of particle aggregation decreases (Fig. 1d).

The degree of aggregation of ZrO₂ particles and their size markedly decrease in the course of a sol-gel process catalyzed by a weak base I. The rate of their formation remains equally high, in contrast to the case of hydrolytic polycondensation of tetramethoxysiliane in the presence of pyridine, when many hours' boiling of the reaction mixture is necessary for hardly discernible SiO₂ particles to be formed. The growth of aggregates of ZrO₂ particles is presumably hindered by competition between the nitrogen atoms of pyridine and water molecules for the coordination sphere of a zirconium atom. An increase in the amount of pyridine in the reaction mixture does not make larger the size of the forming aggregates (Fig. 2), but only decreases the time in which a transparent, slightly opalescent gel is formed from tens of days to 1-2 days.

The formation of comparatively spherical ZrO_2 nanoparticles 100–150 nm in diameter (Fig. 3a) was only observed when a very strong base **IV** was used to catalyze the sol–gel process. In contrast to analogous SiO₂ particles, these nanoparticles have a rather loose structure (Fig. 3a) and, in a short time, disintegrate to give a gel-like structure (Fig. 3b).

CONCLUSIONS

(1) The mechanisms of formation and growth of nanodispersed ZrO_2 and SiO_2 particles synthesized by hydrolytic polycondensation of zirconium and silicon alkoxides in the presence of organic bases are different.

(2) The rate of formation of ZrO_2 particles in the sol-gel process of hydrolytic polycondensation of

zirconium tetraisopropoxide is independent of the basicity of the catalysts used.

(3) The coarsening of the ZrO_2 particles being formed occurs via aggregation of finer particles. This makes impossible synthesis of ensembles of monodisperse ZrO_2 particles in a protonic medium in the presence of organic amines.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 05-03-32818a).

REFERENCES

- 1. Stober, W. and Fink, A., J. Colloid Interface Sci., 1968, vol. 26, pp. 62–69.
- Bogush, G.H., Tracy, M.A., and Zukoski, C.F., IV, J. Non-Cryst. Solids, 1988, vol. 104, pp. 95–106.
- So, Jae-Hyun, Yang, Seung-Man, Kim, C., and Hyun, J.C., *Colloids Surf. A: Physicochem. Eng.* Aspects, 2001, vol. 190, pp. 89–98.
- Sung Kyoo Park, Ki Do Kim, and Hee Taik Kim, *Colloids Surf. A: Physicochem. Eng. Aspects*, 2002, vol. 197, pp. 7–17.
- Khimich, N.N., Zvyagil'skaya, Yu.V., Zhukov, A.N., and Us'yarov, O.G., *Zh. Prikl. Khim.*, 2003, vol. 76, no. 6, pp. 904–908.
- Petrovskii, G.T., Shashkin, V.S., and Yakhkind, A.K., *Fiz. Khim. Stekla*, 1997, vol. 23, no. 1, pp. 43–53.
- 7. Handbook of Sol-Gel Science and Technology, vol. 3:

Applications of Sol-Gel Technology, Sumio Sakka, Ed., Boston: Kluwer, 2005.

- 8. Efremov, I.F., *Periodicheskie kolloidnye struktury* (Periodic Colloid Structures), Leningrad: Khimiya, 1971.
- 9. Hunter, R.J., *Foundations of Colloid Science*, Oxford: Univ. Press, 2001.
- Handbook of Sol–Gel Science and Technology, vol. 1: Sol–Gel Processing, Hiromitsu Kozuku, Ed., Boston: Kluwer, 2005.
- 11. Vaartstra, B.A., Huffman, J.C., Ggadeff, P.S., et al., Inorg. Chem., 1990, vol. 29, pp. 3126-3131.
- Turevskaya, E.P., Kozlova, N.I., Turova, N.Ya., et al., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1995, no. 4, pp. 752–759.
- 13. Clearfield, A., J. Mater. Res., 1990, vol. 5, no. 1, pp. 161–162.
- 14. Larbot, A., Fabre, J.-P., Guizard, C., and Cot, L., J. Am. Ceram. Soc., 1989, vol. 72, no. 2, pp. 257–261.
- 15. Ogihara, T., Mizutani, N., and Kato, M., J. Am. Ceram. Soc., 1989, vol. 72, no. 3, pp. 421-426.
- Bradley, D.C. and Wardlaw, W., J. Chem. Soc., 1951, pp. 280–285.
- 17. Bradley, D.C., Mehrotra, R.C., and Wardlaw, W., J. Chem. Soc., 1952, pp. 2027–2032.
- 18. Perrin, D.D., *Dissociation Constants of Organic Bases* in Aqueous Solutions, London: Butterworths, 1965.
- Iler, R.K., The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica, New York: Wiley–Interscience, 1979.
- 20. Stepin, B.D. and Tsvetkov, A.A., *Neorganicheskaya khimiya* (Inorganic Chemistry), Moscow: Vysshaya Shkola, 1994.