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Synthesis of zirconyl polyolates and their conversion to nanosized zirconia

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Three new methods for the synthesis of zirconyl polyolates by the sol-gel process from zirconyl salts in aqueous media are developed. The polyolates produced are suitable precursors for zirconia nanopowders.

Key words: zirconia, sol-gel technology, polyols, glycerol, nanopowders.

Nanosized zirconia finds application[1] in the production of ceramic oxide electrolytes for fuel cells, technical, refractory and structural bioceramics, abrasives and dyes, plastics and coatings, pharmaceutical and cosmetic formulations, jewellery, *etc.*

The methods used to prepare zirconia nanopowders are commonly classified into two categories, physical and chemical. The former are exemplified by laser-induced evaporation of ZrO_2 (see Ref. 2), and the latter, by precipitation and sol-gel processes. The starting materials for precipitation methods are typically zirconium salts[3], while zirconium propoxide[4,5] and butoxide,[6—8] as well as zirconyl chloride[9,10] or nitrate,[11] for the sol-gel processes.

Zirconium is known[12] to readily form, with the oxygen-containing ligands, complexes stable in aqueous solutions. Hence, such compounds appear as very suitable to be exploited for hydrolysis control (as inhibitors). At the same time, zirconium alkoxides (monoatomic alcohol derivatives) are readily hydrolyzed and thus are used in the sol-gel process conducted in an alcohol medium. This study focuses on the search for moderately hydrolyzable zirconium derivatives that would allow the sol-gel process to be carried out directly in an aqueous solution.

Results and Discussion

1. Synthesis of zirconyl glycerolates by the exchange reaction method. A method for glycerol concentration by precipitating as a complex with zirconium is known.[13] The method was patented rather long ago and has no alternative applications. On the basis of this method, we have developed and implemented the precipitation process for the synthesis of nanosized ZrO_2. First, zirconyl glycerolate was precipitated with an ammonia solution from aqueous zirconyl chloride or nitrate at room temperature or with heating:

$$ZrOX_2 + C_3H_8O_3 \xrightarrow[-NH_4X]{NH_3}$$

$$\longrightarrow ZrOX_n(C_3H_7O_3)_m(C_3H_6O_3)_{(2-n-m)/2},$$

X = Cl or NO_3.

The reaction product, the zirconyl glycerolate gel (ZGG), was dried and calcined. Upon drying, the synthesized ZGG is converted to zirconyl glycerolate xerogel (ZGX) whose calcination yields ZrO_2 nanopowders. In the case of zirconyl chloride, calcination was conducted at 650 °C since at lower temperatures some particles remained unburned (carbonized) due to the presence of chlorine. The results of analysis are given in Table 1.

When using zirconyl nitrate as the starting material, the calcination temperature was 550 °C, no carbonized products were observed. Characteristics of the ZrO_2 nanopowders obtained are listed in Table 2. The size

Table 1. Elemental composition of ZGX derived from $ZrOCl_2$[a]

Entry	T[b]/°C	ZGX composition (%)			Cl : Zr	Yield of ZGX (%)
		C	Cl	Zr		
1	20	18.4	6.9	36.3	0.49	~100
2	70	17.4	5.6	37.1	0.39	~100

[a] $ZrOCl_2 : C_3H_8O_3 = 1 : 2$.
[b] ZGG synthesis temperature.

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Table 2. Specific surface area (*S*) and diameter of particles (*D*) of ZrO_2 nanopowders derived from $ZrO(NO_3)_2$[a]

Entry	T^b/°C	Yield of ZGX (%)	S/m^2 g^{-1}	D/nm
1	20	~100	25	21
2	70	~100	27	19

[a] $ZrO(NO_3)_2 : C_3H_8O_3 = 1 : 2$. Calcination at 550 °C.
[b] ZGG synthesis temperature.

of particles was determined assuming their spherical geometry:

$$D = 3 \cdot 10^{-6}/S\rho ,$$

where D (m) is the particle diameter, S (m^2 g^{-1}) is the specific surface area, ρ (g cm^{-3}) is the material density.

As follows from the data of Table 2, the specific surface area of the final nanopowders increases with increasing the synthesis temperature. As is seen from the micrograph (Fig. 1), the powder is formed by strongly agglomerated particles with the size in the range 20—40 nm.

The above-described synthesis method for nanosized ZrO_2 is comparable to the known[3] process in which zirconium hydroxide is precipitated as a precursor, and the final product has a surface area of ~40 m^2 g^{-1} under the same calcination conditions.

While conducting synthesis with introduction of ammonia or an amine from the gas phase, we found that in this case no precipitate formation took place but, instead, ZGG was formed (in 5 days). The higher the amine basicity (the substitution degree) the smaller the specific surface area of the ZrO_2 powder formed upon ZGG calcination, and, correspondingly, the larger the particle size (Table 3). Thus, ammonia is the base of choice for the sol-gel process.

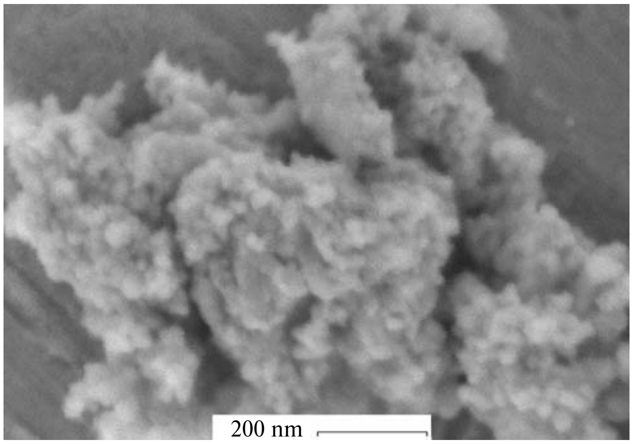

Fig.1. Micrograph of ZrO_2 powder produced by calcination of ZGX synthesized by the method of exchange reactions (see Table 1, entry *2*, S = 27 m^2 g^{-1}). Magnification is 100000.

Table 3. Specific surface area (*S*) and diameter of particles (*D*) of ZrO_2 nanopowders derived from $ZrO(NO_3)_2$ with introducing the amine from the gas phase[a]

Entry	Amine	Yield of ZGX (%)	S/m^2 g^{-1}	D/nm
1	NH_3	~100	31	17
2	CH_3NH_2	~100	10	52
3	$(CH_3)_2NH$	~100	8	65

[a] $ZrOCl_2 : C_3H_8O_3 = 1 : 2$.

2. Synthesis of zirconyl polyolates at the interface of aqueous and organic phases. The results considered clearly indicate that the introduction of a base directly to the water-glycerol solution results in gelation only in the case of ammonia delivered through the gas phase, the gel formation takes several days.

In order to accelerate the process, we suggested to remove ammonium salts by extraction with an organic solvent. As pointed above, the sol-gel process[4] for zirconia nanopowder production makes use of zirconium alkoxides, which can be synthesized only in anhydrous media. If proceed from the accessible zirconyl salts, this approach appears labor-consuming and multistep (typically, four steps):

$$ZrOX_2 \xrightarrow[HCl]{NR^1R^2R^3} [HNR^1R^2R^3]_2ZrX_6 \xrightarrow{ROH}$$
$$\longrightarrow Zr(OR)_4 \xrightarrow{H_2O} Gel \longrightarrow ZrO_2 .$$

It also should be kept in mind that the sol-gel process can be carried out only in an anhydrous alcohol. Zirconium alkoxide could be converted to glycerolate but the complexes formed by glycerol and zirconium are water insoluble. Furthermore, commercial zirconium alkoxides are rather expensive.

The process that we propose includes two steps:

$$ZrOX_2 + HOCH_2CH(OH)CH_2OH \xrightarrow[- HX]{}$$
$$\longrightarrow \underset{Gel}{ZrOX_n(C_3H_7O_3)_m(C_3H_6O_3)_{(2-n-m)/2}} \longrightarrow ZrO_2 .$$

As a result, the acid is extracted into the organic phase, and the water-glycerol solution transforms to the gel:

$$\begin{array}{c}
\dfrac{[ZrOX_2 + C_3H_6O_3]_{aq}}{[NR^1R^2R^3]_{org}} \\
\downarrow \\
\dfrac{[ZrOX_n(C_3H_7O_3)_m(C_3H_6O_3)_{(2-n-m)/2}]_{aq}}{[NR^1R^2R^3HX]_{org}}
\end{array}
\left|\begin{array}{l}\downarrow HX \quad \downarrow Zr^{4+} \quad \uparrow NR^1R^2R^3\end{array}\right.$$

$X = Cl$ or NO_3.

Table 4. Effect of Zr : $C_3H_8O_3$ ratio on ZGX composition[a]

Entry	Zr : $C_3H_8O_3$	ZGX composition (%)			Cl : Zr	Yield of ZGX (%)
		C	Cl	Zr		
1	1 : 0	0	10.2	43.1	0.61	54
2	1 : 1	17.6	5.8	36.7	0.41	74
3	1 : 2	20.2	4.9	36.2	0.35	89
4	1 : 4	27.4	3.6	27.1	0.34	98
5	1 : 6	31.7	2.2	16.8	0.34	~100

[a] Extractant of Cl^--ions is a 15% $NH(C_9H_{19})_2$ solution in chloroform. $ZrOCl_2$: $NH(C_9H_{19})_2$ = 1 : 2. ZGG synthesis time (hereinafter unless otherwise noted) is 30 min.

As can be seen, the reaction of zirconyl salt in aqueous glycerol with an organic base dissolved in an organic solvent consists of the following processes: extraction of the inorganic acid into the organic phase, extraction of the organic amine into the aqueous phase, extraction of zirconium in the form of complexes $(HNR^1R^2R^3)_2ZrX_6$ or $2NR^1R^2R^3 \cdot ZrX_4$ into the organic phase with ZGG formation in the aqueous phase. For the target product to be successfully obtained, optimization of the process conditions is needed.

Optimization of the zirconium : glycerol ratio. Table 4 illustrates the effect of the zirconium : glycerol molar ratio (Zr : $C_3H_8O_3$) in the reaction system

$$ZrOCl_{2\,aq} + C_3H_8O_3 + NH(C_9H_{19})_{2\,org} \longrightarrow$$

$$\longrightarrow ZrOCl_n(C_3H_7O_3)_m(C_3H_6O_3)_{(2-n-m)/2} + NH_2Cl(C_9H_{19})_{2\,org}$$

on the composition of ZGX formed upon ZGG drying.

With the increase in the glycerol mole fraction, the relative content of chlorine in ZGX decreases and the product yield increases. Increasing the glycerol content after the ratio Zr : $C_3H_8O_3$ = 1 : 2 is reached does not result in substantial decerase in chlorine content, while the product yields are still rather high (89—98%) for the Zr : $C_3H_8O_3$ ratios within the range 1 : 2—1 : 4. Accordingly, further increase in amount and hence consumption of glycerol is unreasonable, being virtually of no use for improvement of the quality of the final product.

Selection of the amine for the extraction of anions. In the reaction carried out at the interface, the acid corresponding to the zirconyl salt anion forms the salt with the organic base, *i.e.*, amine, and is extracted into the organic phase:

$$ZrOCl_{2\,aq} + C_3H_8O_3 + NR^1R^2R^3{}_{org} \longrightarrow$$

$$\longrightarrow ZrOCl_n(C_3H_7O_3)_m(C_3H_6O_3)_{(2-n-m)/2} + NR^1R^2R^3HCl_{\,org}\,.$$

In this process, the strength of the base, as well as the length of its hydrocarbon radical, are of substantial importance. To choose the extracting base, we assayed triethylamine, tributylamine, nonylamine, dinonylamine, and a mixture of alkylamines C_{10}—C_{14} and analyzed their effect on the composition of ZGX (Table 5).

The much higher carbon and nitrogen content in samples *1* and *5* as compared to others suggests that triethylamine is strongly extracted into the aqueous solution. Hence, it does not remove acid from the aqueous phase, which is inacceptable. The effciciency of HCl extraction decreases in the series: dinonylamine > nonylamine > tributylamine ≈ amines C_{10}—C_{14}. Being a strong base, dinonylamine provides the minimum chlorine content in ZGX, and owing to its long radical (C : N = 18) it is not extracted into the aqueous phase as evidenced by the zero nitrogen content in ZGX. The product yields obtained with dinonylamine are among the highest of all amines tested.

Selection of synthesis time. In the reaction occurring at the interface, along with the extraction of inorganic acid into organic phase, extraction of zirconium in the form of hexachloro- or hexanitrozirconate of the corresponding amine takes place, which reduces the product yield. Since the extraction of the acid is kinetically faster than the extraction of the metal, the product yield can be optimized by adjusting the synthesis time:

Table 5. Effect of anion-extracting amine ($NR^1R^2R^3$) structure on ZGX composition[a]

Entry	Zr : $C_3H_8O_3$	Amine composition				ZGX composition (%)				Cl : Zr	Yield of ZGX (%)
		R^1	R^2	R^3	C : N	C	N	Cl	Zr		
1	1 : 2	C_2H_5	C_2H_5	C_2H_5	6	29.5	4.2	9.3	22.6	1.06	~100
2	1 : 2	C_{10}—C_{14}	H	H	12	20.0	1.4	4.9	33.5	0.38	92
3	1 : 2	C_4H_9	C_4H_9	C_4H_9	12	20.0	1.3	4.3	31.1	0.35	92
4	1 : 2	C_9H_{19}	C_9H_{19}	H	18	20.2	0	4.9	36.2	0.35	89
5	1 : 4	C_2H_5	C_2H_5	C_2H_5	6	31.7	3.3	12.5	18.0	1.78	99
6	1 : 4	C_4H_9	C_4H_9	C_4H_9	12	30.6	1.5	10.2	16.9	1.55	82
7	1 : 4	C_9H_{19}	H	H	9	27.7	0.5	6.7	28.8	0.60	81
8	1 : 4	C_9H_{19}	C_9H_{19}	H	18	27.4	0	3.6	27.1	0.34	98

[a] $ZrOCl_2$: N(amine) = 1 : 2. Amine concentration 15%. The solvent is $CHCl_3$.

Table 6. Effect of ZGG synthesis time (*t*) on elemental composition of ZGX[a]

Entry	X	*t*/min	ZGX composition (%)				Cl : Zr	Yield of ZGX (%)
			C	N	Cl	Zr		
1	Cl^-	15	30.0	0	4.1	32.1	0.33	73
2	Cl^-	30	27.4	0	3.6	27.1	0.34	98
3	Cl^-	45	31.5	0	3.2	24.7	0.33	60
4	Cl^-	60	30.3	0	4.6	25.0	0.47	31
5	Cl^-	1440	28.9	0	4.5	18.6	0.62	30
6	NO^{3-}	30	26.8	0	0.2	22.4	0.02	87
7	NO^{3-}	1440	28.6	1.2	0	17.6	0	55

[a] $ZrOX_2 : C_3H_8O_3 = 1 : 4$; $ZrOX_2 : NH(C_9H_{19})_2 = 1 : 2$. Dinonylamine concentration 15%. Solvent is $CHCl_3$.

$$ZrOX_{2\,aq} + C_3H_8O_3 + NH(C_9H_{19})_{2\,org} \longrightarrow$$

$$\longrightarrow ZrOX_n(C_3H_7O_3)_m(C_3H_6O_3)_{(2-n-m)/2} + NH_2X(C_9H_{19})_{2\,org}\,.$$

Table 6 lists the data demonstrating the effect of ZGG synthesis time on the final ZGX composition. In the case of zirconyl chloride, the increase in the synthesis time from 15 to 45 min results in a decrease in the chlorine content in the xerogel, and after 45 min the increase in the chlorine content starts. Probably, at this stage chloride in the amine salt undergoes partial replacement by the hexachlorozirconate anion. Correspondingly, the product yields are first increased and then start to decrease, the maximum been attained at the reaction time of 30 min. If the synthesis time lasts for 60 min and longer, the yields are lower considerably. The similar dynamics was observed with zirconyl nitrate.

The effect of solvent. The next optimization step was selection of the organic solvent. The density of the organic phase appreciably affects the character of gelation (Table 7). The lower the solvent permittivity the more efficient the chlorine removal, yet the highest yield was obtained with a solution of dinonylamine in chloroform. In this case, the density of the amine solution is approximately equal to that of the water-glycerol solution of the zirconyl salt, this naturally facilitating dispersion and providing larger phase contact surface. When other solvents were used, ZGG either sedimented or accumulated at the surface. Thus chloroform was a solvent of choice.

Table 8. Effect of dinonylamine concentration in $CHCl_3$ (*C*) on ZGX composition[a]

Entry	*C* (%)	ZGX composition (%)			Cl : Zr	Yield of ZGX (%)
		C	Cl	Zr		
1	5	29.2	5.3	17.0	0.81	93
2	15	27.4	3.6	27.1	0.34	98
3	25	27.8	3.0	22.2	0.35	80

[a] $ZrOCl_2 : C_3H_8O_3 = 1 : 4$, $ZrOCl_2 : NH(C_9H_{19})_2 = 1 : 2$.

Selection of dinonylamine concentration. In the similar manner, the reaction is controlled by the amine concentration in chloroform. The increase in the amine concentration decreases the density of organic phase and the increase in the chloroform content results in its increase. The data on the effect of dinonylamine concentration in chloroform on the characteristics of xerogels obtained are given in Table 8. Chlorine becomes better extractable from ZGG with increase in the amine concentration. However, its increase from 15 to 25% results in a decrease in the yield, most likely due to predominant zirconium transfer in the form of a complex to the organic phase, which is favored by high amine concentration. The optimum dinonylamine concentration is 15% where satisfactory chlorine extraction occurs along with the maximum product yield.

Extraction of xerogels. The as-formed ZGG still contains some residual anions, as well as excess of glycerol. Diethylamine was used to extract these remaining anions and remove nonbound glycerol.

On examining the extraction of ZGX derived from zirconyl chloride, the extraction was found to reduce considerably the chlorine content in ZGX (Table 9, *cf.* entries *1* and *3*). It allows reducing the calcination temperature from 650 to 600 °C for the preparation of ZrO_2 nanopowders from xerogels. Extraction of ZGX also reduces the glycerol concentration. Before extraction, decreasing the zirconium : glycerol ratio results in decrease in the surface area of ZrO_2 nanopowders (increase in particle size). Removal of excess glycerol by the extraction of ZGX results in the increase in the specific surface area at $Zr : C_3H_8O_3 = 1 : 2$ and in its decrease at $Zr : C_3H_8O_3 = 1 : 4$.

Table 7. Effect of organic solvent (with the density, ρ and dielectric constant, ε) on elemental composition of ZGX[a]

Entry	Characteristics of solvent			ZGX composition (%)			Cl : Zr	Yield of ZGX (%)
	Compound	ρ/g cm^{-3}	ε	C	Cl	Zr		
1	CH_2Cl_2	1.33	9.08	30.8	3.8	21.0	0.47	52
2	$CHCl_3$	1.49	4.81	27.4	3.6	27.1	0.34	98
3	CCl_4	1.59	2.24	29.5	0.9	20.1	0.12	70

[a] $ZrOCl_2 : C_3H_8O_3 = 1 : 4$, $ZrOCl_2 : NH(C_9H_{19})_2 = 1 : 2$. Dinonylamine concentration 15%.

Table 9. Effect of extractant on ZGX composition and morphology of ZrO_2 nanopowders (specific surface area, *S* and diameter of particles, *D*)[a]

Entry	Extractant	Zr : $C_3H_8O_3$	ZGX composition (%)			Cl : Zr	S/m^2 g^{-1}	D/nm
			C	Cl	Zr			
1	—	1 : 2	20.2	4.9	36.2	0.35	11	48
2	—	1 : 4	27.4	3.6	27.1	0.34	10	52
3	$(C_2H_5)_2NH$	1 : 2	22.3	—	35.1	—	21	25
4	$(C_2H_5)_2NH$	1 : 4	24.2	0.5	35.8	0.04	6	87

[a] $ZrOCl_2 : NH(C_9H_{19})_2 = 1 : 2$. Solvent is $CHCl_3$.

Table 10. Effect of extractant on ZGX composition and morphology of ZrO_2 nanopowders[a]

Entry	Extractant	Zr : $C_3H_8O_3$	ZGX composition (%)			S/m^2 g^{-1}	D/nm
			C	N	Zr		
1	—	1 : 2	23.4	0.7	29.0	27	19
2	—	1 : 4	26.8	0	22.4	20	26
3	$(C_2H_5)_2NH$	1 : 2	19.5	0.4	38.1	19	28
4	$(C_2H_5)_2NH$	1 : 4	21.6	0.7	37.8	19	28

[a] $ZrO(NO_3)_2 : NH(C_9H_{19})_2 = 1 : 2$. Solvent is $CHCl_3$.

The analogous data for zirconyl nitrate are listed in Table 10. ZGG extraction reduces the specific surface area of the target ZrO_2 powders. As was observed for zirconyl chloride, the decrease in the Zr : $C_3H_8O_3$ ratio resulted in formation of larger ZrO_2 particles. The best results were obtained at the equimolar ratio of zirconium and glycerol. The samples formed had the surface area of 30 m^2 g^{-1}, which is quite sufficient for most applications. Zirconia nanopowders for oxygen-conducting ceramics, produced by laser evaporation have specific surface area of 30—33 m^2 g^{-1}.

Using other polyols for production of zirconia nanopowders. Besides glycerol, there are other polyatomic alcohols that can form organic compounds with zirconium. When we move from ethylene glycol and diethylene glycol to tetraethylene glycol, the product yield increases (Table 11) in the similar manner as with the glycerol content increase (see Tables 4, 9, 10). And again, the particle size of ZrO_2 powder formed after calcination increases. The maximum specific surface area was found for zirconia prepared using glycerol.

On the whole, the general features of formation of zirconyl polyolate gels, as well as nanosized zirconia, in the two-phase systems are as follows:

— the optimum zirconium : polyol ratio (that provides the maximum product yield at minimum polyol consumption) lies in the range 1 : 2—1 : 4;

— the quantitative extraction of anions requires the use of amines containing at least 18 carbon atoms;

— the optimum synthesis time is 15—30 min (if aging lasts for one day or longer, the gel is formed in a much smaller yield);

Table 11. Effect of polyol structure on ZGX composition and morphology of ZrO_2 nanopowders[a]

Entry	Polyol	ZGX composition (%)			Yield of ZGX (%)	S/m^2 g^{-1}	D/nm
		C	N	Zr			
1	Glycerol	23.4	0.7	29.0	80	27	19
2	EG[b]	13.1	1.2	40.5	75	21	25
3	DiEG	18.7	0.9	34.3	77	21	25
4	TriEG	20.9	1.2	32.2	89	16	33
5	TetraEG	27.5	1.1	26.3	85	16	33
6	Glucitol	29.3	0.8	20.2	98	24	22

[a] $ZrO(NO_3)_2$: alcohol = 1 : 2, $ZrO(NO_3)_2 : NH(C_9H_{19})_2 = 1 : 2$. Dinonylamine concentration 15%. Calcination temperature 550 °C.

[b] EG is ethylene glycol.

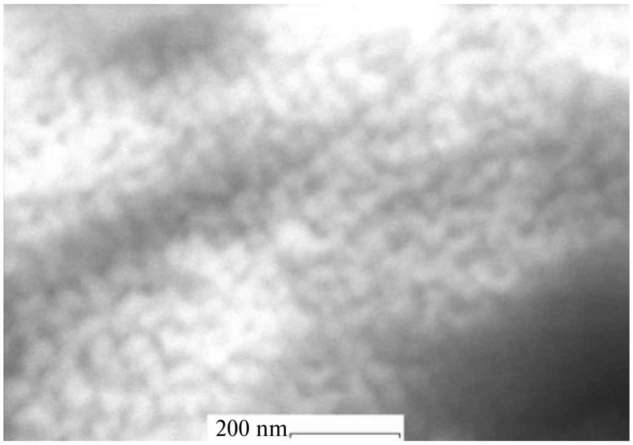

Fig. 2. Microphotograph of ZrO_2 powder produced by calcination of ZGX synthesized by sol-gel process at the interface (see Table 10, entry *1*, $S = 27$ m^2 g^{-1}). Magnification is 100000.

— as organic solvent, chlorinated hydrocarbons showed best, while the amine is taken in such a concentration that to provide equal densities of the aqueous and organic phases;

— extraction of xerogels allows calcination to be carried out at a lower temperature avoiding carbonization of ZGX derived from $ZrOCl_2$ (extraction of ZGX derived from $ZrO(NO_3)_2$ is unreasonable as resulting in the decreased specific surface area of final nanopowders);

— the polyols suitable for the process can be sorted into two groups: those providing maximum product yield (glycerol, glucitol, tri- and tetraethylene glycols) and those providing maximum surface area (glycerol, glucitol).

It should also be mentioned that after the process is finished, the amines used for extraction can be easily regenerated by washing the organic phase with an alkali.

As can be seen from the micrograph of ZrO_2 (Fig. 2) produced from ZGX (see Table 11, entry *1*), the powder is a densely packed structure of nanoparticles with the sizes ranging from 30 to 35 nm.

The sol-gel process developed yields the comparable results (specific surface area of particles is 20—27 m^2 g^{-1}) with the method**[4]** based on hydrolysis of zirconyl isopropoxide, given the gel aging time in both methods is the same. Our method, however, rests on more available starting materials.

3. Oxidative synthesis of zirconyl glycerolates. While examining solubility of zirconyl nitrate in water-glycerol systems, it was found that these solutions are transformed to gels on heating.

Based on this phenomenon, a new method for the synthesis of nanosized zirconia was developed. In aqueous solutions, zirconyl nitrate is known**[14]** to undergo hydrolysis:

$$ZrO(NO_3)_2 + H_2O \rightleftharpoons ZrO(OH)_n(NO_3)_{2-n} + HNO_3.$$

The nitric acid formed can oxidize glycerol ($C_3H_5(OH)_3$) to glyceric acid**[15]**:

$$C_3H_5(OH)_3 + HNO_3 \longrightarrow C_2H_3(OH)_2COOH + NO_2 + H_2O.$$

Thus, in the reaction, some anions NO_3^- are removed leading finally to gel formation:

$$ZrO(NO_3)_2 + C_3H_5(OH)_3 \rightleftharpoons$$

$$\rightleftharpoons ZrO(OH)_n(Y)_m(NO_3)_{2-n-m}\,(\text{gel}) + NO_2\,(\text{gas})$$

$Y = OC_3H_5(OH)_2$ or $C_2H_3(OH)_2COO$.

Gel drying likely involves further hydrolysis as well as glycerol esterification:

$$ZrO(OH)_n(Y)_m(NO_3)_{2-n-m} + H_2O \rightleftharpoons$$

$$\rightleftharpoons ZrO(OH)_k(Y)_{2-k}NO_3 + HNO_3,$$

$$C_3H_5(OH)_3 + n\,HNO_3 \longrightarrow C_3H_5(OH)_{3-n}(NO_3)_n + n\,H_2O\,.$$

Calcination of ZGX is accompanied by explosive decomposition of glycerol nitrates present as an admixture with microflare (microexplosion). As follows from experimental data (Table 12), the resulting ZrO_2 nanopowders are characterized by the same particle size irrespective of Zr : $C_3H_8O_3$ ratio as opposed to the two other methods considered. The ZrO_2 powder is weakly agglomerated spherical particles, 30—35 nm in diameter (Fig. 3).

The oxidative synthesis of ZGG with its subsequent conversion to nanosized ZrO_2 is a particularly advantageous process since it is the simplest, requires neither expensive equipment, nor reagents, nor strictly approved conditions. However, due to a strongly exothermic char-

Table 12. Composition of ZGX produced by oxidation method and morphology of ZrO_2 nanopowders[a]

Entry	Zr : $C_3H_8O_3$	ZGX composition (%)			N : Zr	Yield of ZGX (%)	S/m^2 g^{-1}	D/nm
		C	N	Zr				
1	1 : 2	32.3	0.8	12.8	0.4	~100	24	22
2	1 : 6	31.6	0.8	13.9	0.4	~100	23	23
3	1 : 10	31.6	0.8	7.3	0.7	~100	23	23

[a] Calcination temperature 550 °C.

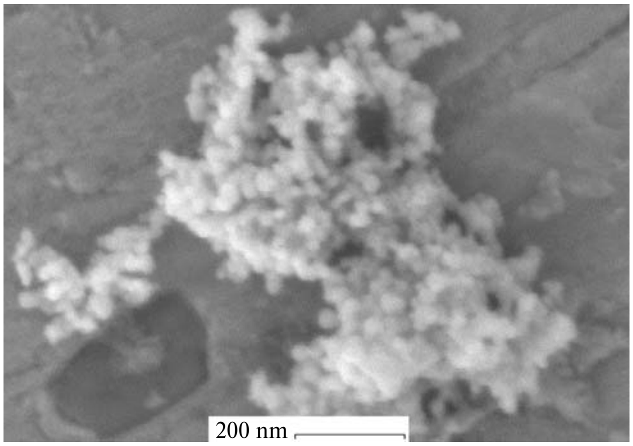

Fig. 3. Microphotograph of ZrO_2 powder produced by calcination of ZGX synthesized by oxidation method (see Table 11, entry *1*, $S = 23$ m^2 g^{-1}). Magnification is 100000.

acter of the calcination reaction, it is not advisable to manufacture the product in large batches.

The ZGX samples were analyzed by IR spectroscopy to explore the effect of synthesis conditions on ZGG formation. Figure 4 shows the IR spectra of ZGX obtained by different methods, as well as of model systems. The Zr—O—C bonds absorption are known**[16]** to lie between 1200 and 1000 cm^{-1}. There are strong absorption bands due to glycerol in this region (see Fig. 4, *1*). The spectrum of a zirconia nanopowder dispersed in glycerol (see Fig. 4, *2*) shows the same bands. In the IR spectrum of ZGX produced using precipitation (exchange reaction) method (see Fig. 4, *3*) there are two absorption bands at 1098 and 1039 cm^{-1}, the former being more intensive. The same two bands with equal intensities are present in the spectrum of ZGX produced at the interface at Zr : $C_3H_8O_3$ = 1 : 2 (spectrum *4*). In the IR spectrum of ZGX produced by the oxidative process (spectrum *5*), the band at 1039 cm^{-1} is more intensive. Spectrum *2* is almost equivalent to spectrum *5*. The band shape in the spectrum *4* is intermediary between the spectra *3* and *5*. Thus, presumably, the gelation at the interface yields glycerolate first, which is followed by its partial hydrolysis. ZGG formation in the oxidative process is due to hydrolysis only. This conclusion is also confirmed by the spectrum *6* of ZGX obtained at the interface at Zr : $C_3H_8O_3$ = 1 : 4. This spectrum is virtually identical to the spectrum *3* of ZGX since in excess of glycerol hydrolysis is slowed down. Certain changes in the spectra are observed in the 600—400 cm^{-1} region, which is characteristic of Zr—O—Zr, Zr=O, and Zr—OH vibrations. These changes, however, are not very informative because of using zirconyl alkoxides rather than zirconium alkoxides as the starting materials.

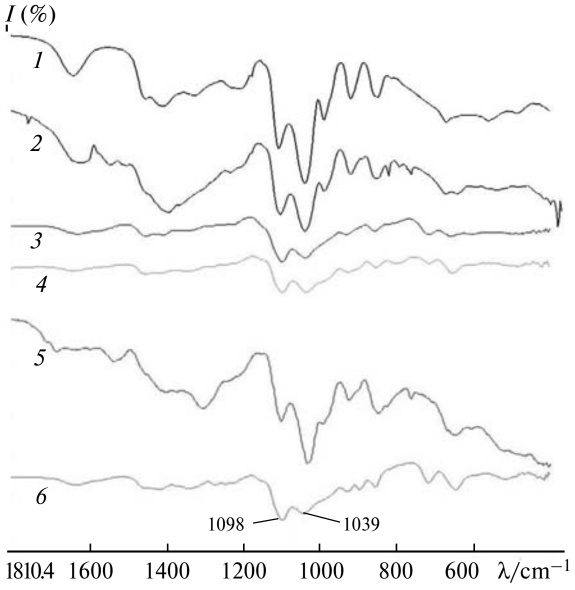

Fig. 4. IR spectra of glycerol (*1*); nanosized ZrO_2 dispersed in glycerol (*2*); ZGX prepared by the precipitation method of exchange reactions (*3*), sol-gel process at the interface at Zr : $C_3H_8O_3$ = 1 : 2 (*4*), oxidative method (*5*), sol-gel process at the interface at Zr : $C_3H_8O_3$ = 1 : 4 (*6*).

The results discussed demonstrate that the developed methods for synthesizing nanosized ZrO_2 *via* zirconyl polyolates can easily be realized in aqueous medium with available reagents. In all cases, the ZrO_2 powder formed upon polyolate calcination was free of carbon, nitrogen and chlorine. Therefore, no elemental analysis data for each individual sample are presented.

The chemical methods for the synthesis of nanooxides are much cheaper than the physical ones. Nonetheless, the quality of resultant oxide ceramics being the criterion for choosing the production process, the goals of further research can be specified only after detailed analysis of different methods.

Experimental

Elemental analysis was carried out on a Perkin Elmer elemental analyzer. For IR spectra, Perkin Elmer IR/FTIR Spectrum One spectrometer was used. The surface area for zirconia powders was measured using the BET technique of gas (nitrogen) adsorption, with a TriStar 3000 V.6.03A analyzer. The instrument for micrographs was the LEO 982 electron scanning microscope.

Synthesis of ZGG by precipitation method. Zirconyl nitrate (9.94 g, 0.0043 mol) was dissolved in 3 mL of water. Then glycerol (0.31 g, 0.0086 mol) was added. The mixture was stirred until its homogenization. To the homogeneous mixture, 25% ammonia solution (5 mL) was added dropwise at 20 °C. The same procedure was performed at 70 °C. The mixture was stirred for 5 min. The precipitate obtained was washed with water to neutral pH of wastewater.

Synthesis of ZGG by the method of exchange reactions (from the gas phase). Zirconyl nitrate (5.00 g, 0.021 mol) was dissolved in 3 mL of water. Then glycerol (3.98 g, 0.043 mol) was added with stirring. Another beaker (volume 200 mL) with 5 mL of 25% ammonia solution was held with the former in the closed space for 5 days.

Synthesis of ZGG by the sol-gel process at the interface. Zirconyl chloride (or nitrate) (0.0062 mol) was dissolved in 2 (or 4 mL) of water. Then the required amount of glycerol or other polyol was added. The mixture was homogenized by stirring, then the amine dissolved in the organic solvent was added (the ratios are given in Tables). After gel was formed (no more stirring could be performed) the pure solvent (25 mL) was added to the mixture, which was further stirred magnetically for additional 5 min. The gel that formed was filtered through the kapron net, then put in the beaker and stirred with 20 mL of chloroform to remove residual amine, which was followed by second filtration and washing with 15 mL of chloroform.

Synthesis of ZGG by the oxidative method. Zirconyl nitrate (9.94 g, 0.0043 mol) was dissolved in a saturated water-glycerol solution at varied Zr : $C_3H_8O_3$ ratios. The mixture was heated until the gel was formed.

Synthesis of ZGX from ZGG. The zirconyl glycerolate gels were dried at 70 °C to constant mass.

Extraction of xerogels. Xerogels were placed in an extractor for extraction with hot solvent, and subjected to extraction with diethylamine for 24 h.

Synthesis of ZrO_2 by ZGX decomposition. Xerogels were placed in the ceramic plates and calcined in a muffle (the temperature is given in Tables).

References

1. T. E. Konstantinova, I. A. Danilenko, V. V. Tokii, V. A. Glazunova, *Ot novatsii k innovatsii* [From discovery to innovation], *Nauka i innovatsii* [*Science and Innovations*], 2005, **1**, 76 (in Russian).
2. Yu. A. Kotov, V. V. Osipov, O. M. Samatov, M. G. Ivanov, V. V. Platonov, A. M. Murzakaev, E. I. Azarkevich, A. I. Medvedev, A. K. Shtolts, O. R. Timoshenkova, *Techn. Phys.*, 2004, **49**, 352.
3. D. Tichit, D. E. Alami, F. Figueras, *Appl. Cat. A: General.*, 1996, **145,** 195.
4. G. K. Chuah, S. H. Liu, S. Jaenicke, J. Li, *Microporous and Mesoporous Materials*, 2000, **39**, 381.
5. A. Aronne, A. Marotta, P. Pernice, M. Catauro, *Thermochim. Acta*, 1996, **275**, 75.
6. X. Bokhimi, E. Munos, J. L. Boldu, E. Adem, O. Novaro, *J. Sol-Gel Sci. Technol.*, 2000, **17**, 219.
7. S. Kim, S. W. Nam, S. Yoon, S. Hyun, J. Han, T. Lim, S. Hong, *J. Mat. Sci. Lett.*, 2004, **39**, 2683.
8. R. Gomez, T. Lopez, X. Bokhimi, *J. Sol-Gel Sci. Technol.*, 1998, **11**, 309.
9. J. Shen, Q. Zhang, J. Wang, T. Yang, Z. Deng, B. Zhou, L. Chen, *J. Sol-Gel Sci. Technol.*, 2000, **19**, 271.
10. O. Vasylkiv, Y. Sakka, *Scr. mater.*, 2001, **44**, 2219.
11. G. Stefanic, S. Popovic, S. Music, *Termochim. Acta*, 1997, **303**, 31.
12. A. A. Grinberg, *Vvedenie v khimiyu kompleksnykh soedinenii* [Introduction to the Chemistry of Complexes], Khimiya, Moscow, 1971, 632 pp. (in Russian).
13. DE Pat. 501110; *Chem. Abstrs.*, 1998.
14. W. B. Blumenthal, *The Chemical Behavior of Zirconium*, Princeton: Van Nostrand, 1958.
15. A. N. Nesmeyanov, N. A. Nesmeyanov, *Nachala organicheskoi khimii* [Elements of Organic Chemistry], Khimiya, Moscow, 1970, 824 pp. (in Russian).
16. F. Rubio, J. Rubio, J. L. Oteo, *J. Mat. Sci. Lett.*, 1998, **17**, 1839.

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