

Hydrothermal Synthesis of Steady-State Zirconium (IV) Oxide

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Abstract Influence of admixtures of yttrium (III) oxide and adipic acid on phase composition and extraction degree of zirconium (IV) oxide in the process of hydrothermal treatment of aquatic solution of zirconium (IV) oxychloride is studied.

Keywords Hydrothermal Synthesis, Zirconium (IV) Oxychloride, Yttrium (III) Oxide, Adipic Acid

1. Introduction

Steady - state zirconium (IV) oxide is widely used in the production of ceramics, refractories, catalysts and adsorbents, fuel elements (power rods) for nuclear power plants and as a basic constituent in the production of fuel cells [1]. In the technology of producing there exists the concept of “stabilization” that means introducing rare earth metals into the lattice of zirconium (IV) oxide to avoid its transition from monoclinic into tetragonal modification.

Ukraine occupies the first place in Europe and the third place in the world for the supplies of zircon - one of natural minerals of zirconium. The content of zirconium (IV) oxide in this mineral makes up more than 65%. There are different ways of obtaining zirconium (IV) oxide from natural raw material in industry [2,3].

The requirement of industry in high-quality zirconium-containing materials is increasing. One of above mentioned materials appears to be zirconium (IV) oxychloride. Its basic application is the use as a reagent for obtaining oxide and steady-state oxide of zirconium (IV) oxide for the electrolyte of fuel elements, catalysts and adsorbents. One of perspective methods is known to be hydrothermal one. This method enables to influence actively the formation of Zirconium compounds with the preset phase and chemical composition [4]. Among numerous types of hydrothermal synthesis of the steady-state zirconium (IV) oxide the synthesis from aquatic solutions of Zirconium inorganic salts is mostly worthy of notice. Therefore, further investigation was

aimed at studying the process of zirconium (IV) oxide stabilization by yttrium (III) oxide in presence of organic acids.

2. Materials and Methods

Zirconium (IV) oxychloride $ZrOCl_2 \cdot 8H_2O$, distilled water, yttria (III) and adipic acid were used as initial reagents. Researches of the process for producing zirconium (IV) oxide from solution of zirconium (IV) oxychloride were conducted in an autoclave in the temperature range of 373 - 673 K, at pressure of 1 - 2 MPa during two hours. Influence of admixtures of yttria (III) and adipic acid was investigated by adding them to the solution of zirconium (IV) oxychloride under mixing, in an amount 0,5 - 1 g and 0,1 - 0,5 mole per 1 mole of zirconium (IV) oxide correspondingly, before the stage of hydrothermal treatment. The concentration of zirconium (IV) oxide in the solution of zirconium (IV) oxychloride was determined by complexometric method [5]. Products of hydrothermal treatment of zirconium (IV) oxychloride solutions were dried at temperature 423 K and calcined at - 873 K during two hours. The phase analysis of hydrothermal synthesis products was performed by means of X-ray photography diffractometer *DRON - 2.0* using a monochromatic cobalt radiation. Photomicrographs of samples were got by means of electronic raster micro analyzer *REMMA 102-02*. Concentration of monoclinic and tetragonal phases of was determined from relative intensities of two most intensive peaks of monoclinic phase ($2\theta_1 = 28.30^\circ$ - is a plane (111), $2\theta_2 = 31.55^\circ$ - is a plane (11 $\bar{1}$); radiation Co-K α , $\lambda = 1.5405 \text{ \AA}$) and one of tetragonal phase ($2\theta = 30.55^\circ$ - is a plane (111)) by a formula:

$$x_t, \text{mass.}\% = - \frac{I_t(111)}{I_m(111) + I_t(111) + I_m(11\bar{1})} \times 100 \quad (1)$$

where I_m and I_t are intensities of diffraction maxima in the corresponding planes of monoclinic and tetragonal phases [5].

Degree of zirconium extraction (α , %) from solution into sediment were calculated by the following formula:

$$\alpha = \frac{C_1 - C_2}{C_1} \cdot 100, \quad (2)$$

where α – extraction degree of zirconium (IV) oxide from solution, %;

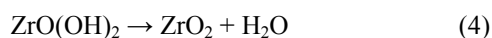
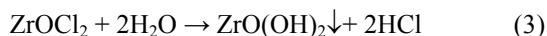
C_1 – theoretical concentration of zirconium (IV) oxide in solution, g/l;

C_2 – concentration of zirconium (IV) oxide in solution in set time, g/l.

3. Results and Discussion

The hydrothermal synthesis of zirconium (IV) oxide from aquatic solutions of zirconium (IV) oxychloride proceeds in two stages:

- 1) thermohydrolysis of zirconium (IV) oxychloride with the formation of oxohydrated Zirconium compounds (3);
- 2) dehydration of these compounds with the formation of amorphous or crystalline zirconium (IV) oxide (4):



At hydrothermal treatment of clean solutions of zirconium oxychloride, products of hydrolysis are found to be fine-grained powders of zirconium (IV) oxide with monoclinic crystalline structure (Fig. 1).

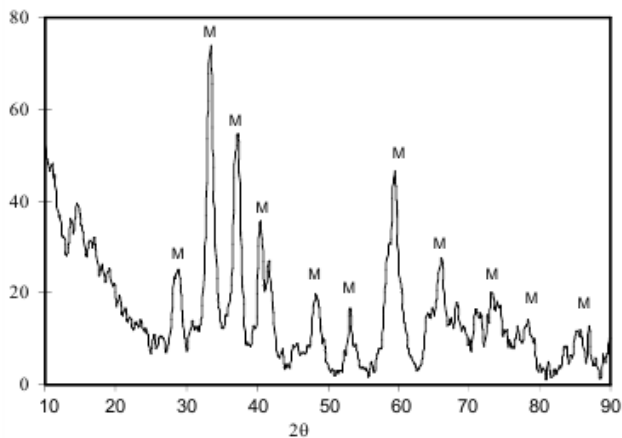


Figure 1. X-ray diffractogram of hydrothermal treatment products of zirconium oxychloride aquatic solution after calcination at 873 K, M - ZrO_2 – monoclinic modification

When yttrium (III) cations are introduced into zirconium (IV) oxychloride, products of hydrothermal treatment of solutions consist mainly of zirconium (IV) oxide of tetragonal modification [6,7] with the insignificant admixtures of monoclinic zirconium (IV) oxide (Fig. 2). However, we can observe the growth and arrangement of primary crystallites.

Hydrothermal synthesis of zirconium (IV) oxide in

presence of organic acids is that organic substances form stronger complexes with zirconium ions and are absorbed on the surface of zirconium (IV) hydroxide particles thus markedly affecting the morphology and crystallization of zirconium (IV) oxide particles [8]. In the above mentioned work the influence of adipic acid on phase and dispersible composition of hydrothermal synthesis products of steady-state zirconium (IV) oxide was studied.

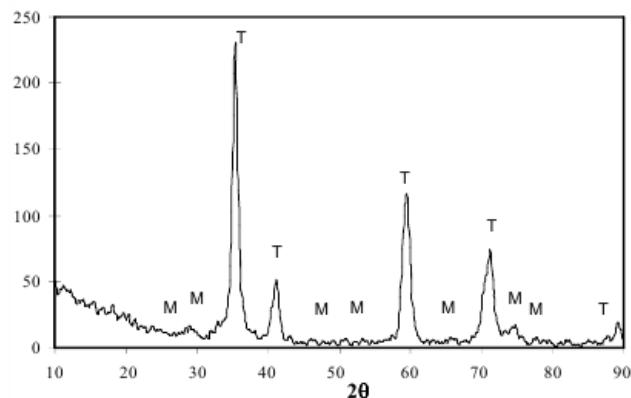


Figure 2. X-ray diffractogram of hydrothermal treatment products of aquatic solution of zirconium (IV) oxychloride with additions of yttrium (III), calcinated at 873 K, M - ZrO_2 – monoclinic modification, T - ZrO_2 – tetragonal modification

Analysing the results of X-ray analysis of hydrothermal synthesis products (Fig. 3) showed that the powders obtained were the crystallized structure of zirconium (IV) oxide (with tetragonal modification).

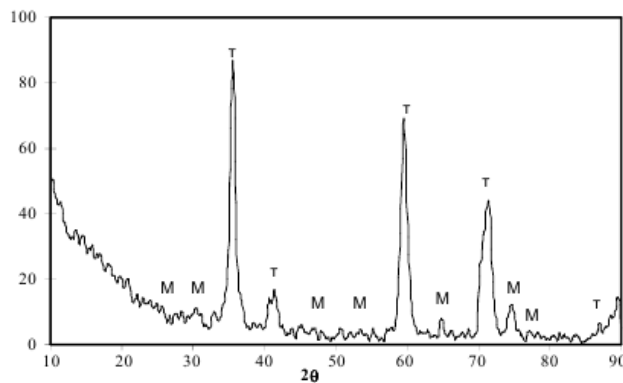


Figure 3. X-ray diffractogram for products of hydrothermal treatment of aquatic solution of zirconium oxychloride with additions of yttrium (III) and adipic acid, calcinated at 873 K, M - ZrO_2 – monoclinic modification, T - ZrO_2 – tetragonal modification

Data obtained from X-ray researches are processed by formulas (1, 2) and tabulated in Table 1. From the presented tabular data it is evident that the concentration of zirconium (IV) oxide tetragonal phase is between the limits 0 and 97.5%; degree of Zirconium extraction from solution of its oxychloride is from 95.5 to 99.8%. Introducing adipic acid to the system results in the increase of zirconium (IV) oxide tetragonal phase concentration (97.5%) and degree of zirconium (IV) oxide extraction from oxychloride solution

(99.8%).

In order to determine distribution of elements on the surface of the obtained product, at the synthesis of which yttrium (III) oxide and adipic acid were used, X-ray microanalysis was conducted [9]. Photomicrograph (Fig. 4) and analysis of a sample in points 1-5 showed identical chemical composition which is presented in Table 2.

The average particle size distribution is shown in Fig. 5.

Table 1. Phase composition and degree of zirconium (IV) oxide extraction at hydrothermal treatment of zirconium (IV) oxychloride solutions

Type of sample	Phase concentration of zirconium (IV) oxide, %		Zirconium (IV) oxide extraction degree (α ,%)
	m - ZrO ₂	t - ZrO ₂	
ZrOCl ₂	100	–	95.5
ZrOCl ₂ + Y ₂ O ₃	5	95	96.3
ZrOCl ₂ + Y ₂ O ₃ + adipic acid	2.5	97.5	99.8

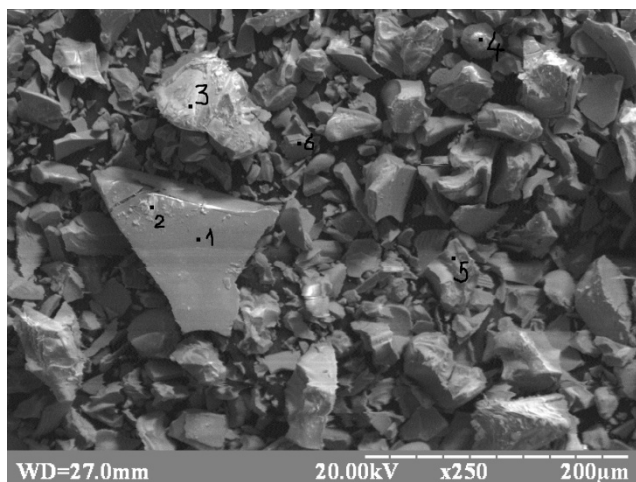


Figure 4. Photomicrograph showing the product of hydrothermal treatment of aquatic solution of zirconium (IV) oxychloride with addition of yttrium (III) oxide and adipic acid

Table 2. Micro-X-ray analysis of a sample in points 1-5.

Element	Sr	Intensity	Error	C_Conc
Si	K	2132.00	10.23	1.63
Cl	K	375.00	36.98	1.41
Y	K	-8.00	47.08	0.00
Y	L	4652.00	7.45	18.23
Y	M	-366.00	33.46	0.00
Zr	K	-10.00	30.93	0.00
Zr	L	17663.00	2.47	78.73
Zr	M	677.00	19.65	0.00
Summ				100.00

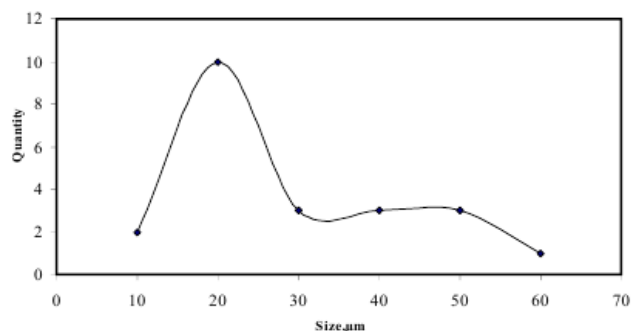


Figure 5. The average particle size distribution

In accord with the obtained dependence, it is possible to conclude that mainly the particles of the product are presented 20 µm in size.

4. Conclusion

It is determined that at hydrothermal treatment of aquatic solutions of zirconium oxychloride maximum concentration of tetragonal phase of zirconium dioxide and degree of zirconium dioxide extraction is observed for the sample containing yttrium (III) oxide and adipic acid admixtures, at the temperature of hydrothermal synthesis of 573 K. In the given sample distribution of substances on a surface is uniform. Prevailing size of particles is 20 µm.

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