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Characteristics of selected methods for the synthesis
of nanometric zirconium oxide − critical review

Charakterystyka wybranych metod syntezy
nanometrycznego tlenku cyrkonu − przegląd

Abstract

High chemical stability, resistance to changes in the pH, pressure and temperature meant that zirconium
oxide is widely used in many fields. It is used in water treatment and waste water treatment processes, as
well as air purification. In this paper, selected methods of nano-zirconia synthesis in liquid phase were
characterized. These methods include, among others, the microemulsion method. Based on literature
data, the advantages and difficulties associated with the use of each method are presented, in order to
answer the question of which method of nanometric zirconium oxide synthesis in the liquid phase is the
most advantageous. The authors also pointed out some directions of development for the discussed
methods, which relate to, among others, solvent change and the use of additives in the form of polymers.

Keywords: nano zirconia, hydrothermal method, synthesis, microemulsion method

Streszczenie

Wysoka stabilność chemiczna, odporność na zmiany pH, ciśnienia i temperatury sprawiły, że tlenek
cyrkonu znajduje szerokie zastosowanie w wielu dziedzinach. Jest stosowany w procesach uzdatniania
wody i oczyszczania ścieków, a także w oczyszczaniu powietrza. W niniejszej pracy scharakteryzowano
wybrane metody syntezy nanotlenku cyrkonu w fazie ciekłej. Wśród grupy tych metod wyróżnia się m.in.
metodę mikroemulsji. Na podstawie danych literaturowych przedstawiono zalety i trudności związane
ze stosowaniem poszczególnych metod, aby móc odpowiedzieć na pytanie, która metoda syntezy
nanometrycznego tlenku cyrkonu, w fazie ciekłej, jest najkorzystniejsza. Autorzy wskazali również na
pewne kierunki rozwojowe omówionych metod, które wiążą się m.in. ze zmianą polarności rozpuszczalnika
i stosowaniem dodatków w formie polimerów.

Słowa kluczowe: nanotlenek cyrkonu, metoda hydrotermalna, synteza, metoda mikroemulsji

1. Introduction

Special properties of zirconia and its wide application mean that methods of its preparation are constantly being developed. The direction of this expansion results from the need to obtain materials with improved performance associated with the mechanical and thermal strength, and chemical stability.

Nano-sized zirconia can be obtained in both the gas and liquid phases, as well as from the solid. There are two general groups of methods for obtaining nanomaterials. These methods are "bottom-up" and "top down" [1–3]. "Bottom-up" methods rely on building a nanometric structure from below, that is, from the level of individual atoms or molecules. "Top down" methods, as methods from above, rely on grinding a solid on a micrometer structure to nanometer sizes 15). Methods of synthesis in the gaseous and liquid phases are among the "bottom-up" methods, and methods of synthesis in the solid state, in most cases, are classified as "top down" methods. Solid state synthesis, exemplified by mechanochemical synthesis, is based on the fact that chemical reactions are induced by mechanical energy. Whereby there is a reduction in the temperature of a chemical reaction [4–6].

2. Synthesis of nanometric zirconia in the vapor phase

Methods of synthesis in the gaseous phase are divided into physical vapor deposition PVD [7], which involves the condensation in an inert gas [8], and chemical vapor deposition CVD [9–12]. In this method, volatile compounds are heated to form vapor, mixed and transported using a carrier gas to a substrate, on which surface crystallization of the product takes place. In these methods, due to the determination of the appropriate conditions, the pair (usually oversaturated) becomes thermodynamically unstable, and therefore the formation of the condensed phase by homogeneous nucleation of solid phase occurs. The process is carried out with a high degree of vapor supersaturation resulting in an increased density of nucleation during the growth of nucleating agents. The key issue to achieve nanometric product is a fast extinguishing system, completed within a reasonable time, which is done by removing the source of supersaturation or extending the kinetics (cooling circuit), with the result that the particles do not grow [3].

Among these methods, various techniques for depositing material from a gaseous phase are highlighted. For example, it may be a magnetron sputtering [13, 14], plasma spraying [15–20], which consists in creating a plasma of high temperature, to 2000 K, and then delivered thereto, by a carrier gas, the material in the form of a powder that will be deposited. Hass et al. [15] concluded that a ceramic coating obtained this way may exhibit less consistency with the substrate and be characterized by higher porosity and non-uniform distribution of the pore volume fraction and shape. This fact significantly affects the thermal conductivity of the material. For another technique, which is the electron beam – physical vapor deposition (EB-PVD), the elements are rotated in the vapor plume, so that condensation of vapor molecules generally occurs unevenly. The result is a layer consisting of a porous, strongly

textured columnar structures of different lengths. Such a layer structure favors its flexibility and increases the thermal conductivity. Another example of physical vapor deposition is an electron beam – directed vapor deposition (EB-DVD) in which the material is not rotated. This results in a layer with a columnar structure, but with similar porosity, shape and length [15]. There is also a technique, which uses stellarator, specifically heliotron, known as the solar physical vapor deposition (SPVD) method [21].

Phase synthesis methods require specific gas pressure and temperature. Therefore, it is necessary to use specific and expensive equipment as well as facilities, among which plasma burners and magnetron stand out [13].

Methods for chemical synthesis from the gas phase can also be divided into several techniques. It should be noted that these methods differ mainly in the way of introducing the precursor and in the type of thermal energy source. In this group, chemical synthesis in the gaseous phase with the use of organometallic precursors [11, 22], liquid-injection chemical vapor deposition [23] and vapor phase hydrolysis [24] can be distinguished. And in the case, where the precursor is not introduced in the form of a vapor, but in the form of tiny droplets generated by a nebulizer, e.g. ultrasonic, spray pyrolysis techniques [25, 26] are highlighted, as well as others, e.g. aerosol assisted chemical vapor deposition (AACVD) [27].

Methods of synthesis and deposition from the gaseous phase result in the acquisition of a material with high purity. They allow to obtain the product, both in powder form and in the form of a layer applied to the substrate. The biggest limitation in the application of these methods is the need to use expensive and complex equipment.

3. Examples of the synthesis of nanometric zirconia in the liquid phase

Among liquid-phase synthesis methods, inter alia co-precipitation [28–31], hydrothermal methods [32–42], sol-gel method [43–48] and microemulsion method [49–56] are distinguished.

3.1. Synthesis of nano-zirconia by co-precipitation

Co-precipitation methods can be classified as conventional methods for the preparation of nanocrystals. Depending on the reaction conditions and substrates, the method allows to obtain particles with different diameters. Crystalline, non-agglomerated, nano-sized Al_2O_3-ZrO_2 prepared by Zhou and coworkers [57] can be cited as examples, which had a particle diameter of about 7 nm, followed by tetragonal zirconia polycrystals stabilized by yttrium (3 mol%.) with a diameter of 21.3 nm obtained by Hsu et al. [58] as well as lead catalysts based on CdO_2-ZrO_2 (in a single phase) with a diameter of 5.2 to 28.9 nm [59] and the Y_2O_3-ZrO_2 powder with a crystal diameter of 53–109 µm obtained by Aruna et al. [60].

The greatest advantage of the precipitation method is the possibility to obtain the product in amounts consisting of grams [28], and the ability to use cheaper and easier to

acquire equipment and nano-particle precursors [58, 61]. The disadvantage of this method is the inability to control the size of the resulting nanoparticles [28]. In order to reduce the agglomeration of nanoparticles, Wang et al. [61] proposed the synthesis of nano-ZrO_2 based on the direct precipitation using ethanol instead of water. The authors [61] used water, ethanol and water-ethanol mixtures at various ratios by volume, $ZrOCl_2$ i $NH_3 \cdot H_2O$, except that the surfactant was applied in the form of poly(ethylene glycol) 800 – PEG 800. Depending on the solvent used, products with different grain size and dispersion were obtained. The authors [61] have shown that the use of ethanol-limited agglomeration of particles, and no addition of PEG 800, additionally increase this effect [61].

3.2. Synthesis of nano-zirconia by hydrothermal methods

Hydrothermal methods are a group of methods among which hydrothermal decomposition, hydrothermal crystallization, homogeneous hydrothermal precipitation, microwave hydrothermal synthesis and hydrothermal synthesis, assisted by ultrasound and also hydrothermal synthesis under supercritical conditions [62] as well as hydrothermal oxidation [35] are highlighted. Hydrothermal methods relate to processes at hydrothermal conditions, which depend on temperature, pressure, pH, redox potential and environmental activity of the ingredients, which depends on the dielectric constant and the dissociation of water [35, 62]. It should be emphasized that, already in 1980, using the hydrothermal method, nanocrystalline powders based on ZrO_2 were obtained.

The hydrothermal method can be based on crystallization in an aqueous solution under increased pressure and at a temperature below the critical point of water. This process is conducted in an autoclave, where the substance concentration gradient is determined. The aterial is arranged in the lower part of the autoclave. This material is heat-solubilized, then travels up through the autoclave wherein at a lower temperature, due to the saturation of the solution, the crystallization of crystals occurs. Hydrothermal synthesis refers to synthesis of a compound in the hydrothermal solution under the influence of temperatures above 100°C and at a pressure above 1 atmosphere. For the synthesis of zirconium oxide (IV), the essence of the method is the production of ceramic sols, by chemical reaction in an aqueous or organic-aqueous solution, while applying heat and pressure, in the presence of an alkali or acid, which have a pseudo catalytic effect on the reaction [37]. Hydrothermal synthesis allows to obtain the three crystalline forms of zirconium oxide (IV): monoclinic, tetragonal [35] and the cubic [37], at the same time, with a lower rate of the monoclinic form. Depending on the reactants and conditions of the synthesis, it is possible to obtain particles with different diameters. The impact of metal precursors is significant, which has been demonstrated by the Caillot and co-workers [63] and derived by their surface characteristics and ICP analysis results compiled (based on [63]) and reported graphically in Figure 1. Based on the graph, it can be concluded that the addition of cerium, lanthanum and titanium resulted in an increase in the surface area of the zirconia products. However, it should be emphasized that this increase was not identical with the increasing proportion of each metal oxide in the final product.
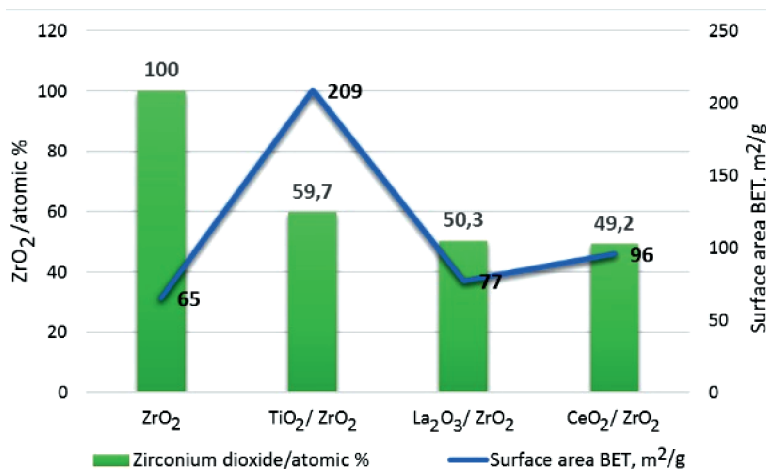
Fig. 1. Effect of metal precursor addition on the surface area of zirconia, on the basis [63]

Hydrothermal methods have both advantages and disadvantages. Among the advantages of these methods, we must distinguish the ability to conduct the process at low temperatures (max. 374oC), no need for a thermal treatment at high temperatures, high purity and quality of the products obtained, a small dispersion particle size, the ability to control the shape of the grains and nucleating agents. The increase in nucleation may be controlled by varying the concentration, increasing or decreasing the hydrolysis temperature and also increasing the duration of hydrolysis as well as by the introduction of surfactants during dehydration and changes in pH [62]. In contrast, the disadvantages of the hydrothermal methods include a high degree of complexity of the apparatus and its cost, as well as an inability to direct the observation of the process.

The microwave hydrothermal method, also called the solvothermal method, is a type of hydrothermal methods, which use microwave energy as a heat source. As a result, the reaction mixture does not have direct contact with the heating element and the time of whole process is considerably reduced. With the increase in pressure, the particles diameter increases and the monoclinic phase content in the product decreases. The result of the process is obtaining a material of high purity whose grain diameter is in the range of 5–50 nm [41, 42].

3.3. Synthesis of nano-zirconia by the sol-gel method

Another example of methods for the synthesis of nanometric zirconia is the sol-gel method. This type of chemical synthesis based on the specific chemical reactions taking place in solution, and in a further step on a series of transformations starting solution – first in the form of sol, then gel, ending with the conversion of the gel into a solid amorphous or crystalline structure [43, 44]. Therefore, this method is used to produce glass [45, 64, 65]. The conversion of the sol into gel is based on a dehydrated colloidal solution of material hydroxide particles, thereby producing a gelatinous substance, called the gel. These reactions are often carried

out with the use of alkoxides of various elements as starting materials [43]. In this case, the formation of a sol – gel system based on the hydrolysis and condensation reactions. The first reaction taking place in solution comprises of the hydrolysis (breakup) of alkoxy bond in the molecule Me-OR and the creation of hydroxyl bonds Me-OH. This reaction precedes in a mutual solvent for the alkoxide and water, with the participation of a suitable catalyst. This is followed by a condensation reaction between hydroxyl and alkoxy groups or two hydroxyl groups, resulting in the formation of bond type $(RO)_{n-1}Me\text{-}O\text{-}Me(OR)_{n-1}$, where n is the number of alkoxy groups in the molecule of alkoxide. The hydrolysis and condensation reactions occurring in parallel result in an increase in the number of Me-O bonds, which leads to initiation of the gelation process. The course of the described reaction depends on the temperature, pH, water and solvent content, polarity of the solvent, and type and concentration of the used catalyst. The catalysts, which are used in the sol-gel method, may be acidic or alkaline. In the first case, inorganic or organic acids are used, and in the second, it is mostly ammonium hydroxide. The increase in the number of Me-O bonds is the cause of the partial polymerization of alkoxides, which subsequently agglomerate. This results in an increase in the viscosity of the system, which, during prolonged drying, is converted to a gel by evaporation of the solvent [43]. In further steps, calcination is carried out.

The advantages of the sol-gel process include simplicity of use and low equipment cost, high purity raw materials and a high degree of homogeneity of the microstructure, the relatively low process temperature in comparison with synthesis methods from the gas phase like PVD (Physical Vapour Deposition) and CVD (Chemical Vapour Deposition), no toxic waste or its low participation, as well as the ability to receive color layers [43, 44]. In contrast, the disadvantages of this method include the high cost of chemical reagents, as well as what is one of the key issues – stability of technological parameters [43].

The sol-gel method is often used to receive various types of ceramic coatings. For the preparation of nanocrystalline sulfated zirconium oxide (IV), the process can be carried out in two stages. In the first step, hydrolysis and condensation take place, and in the second, sulfation with sulfuric acid or ammonium sulfate occurs. Whereas in a one-step method, the mentioned chemical reactions take place simultaneously [46]. The one-step synthesis method proposed by Mishra and colleagues [46] allowed to obtain a product with a particle diameter of 11–16 nm, specific surface area of 101–118 m^2/g and a diameter and pore size that were respectively 0.152–0.190 cm^3/g and 58–62 Å. These parameters (except for the diameter and pore size) are not very different from those, which characterize the product obtained by the two-step method. Particle diameter, surface area, pore diameter and pore size of the sulfated zirconium oxide (IV) were, respectively, 11 nm, 101 m^2/g, 0.087 cm^3/g and 37 Å [46]. All the obtained products were characterized by a tetragonal structure. Akkarin et al. [47], using the sol-gel method, have received nanocrystalline sulfated zirconium oxide (IV) on mesoporous silica used as a carrier. Zirconium acetylacetonate and tetraethyl orthosilicate were used as reactants. The sulfation reaction was carried out using *in situ* H$_2$SO$_4$. The authors [47] have also studied the effect of the amount of sulfuric acid added, as the S/Zr mole fraction, on structural properties. It has been shown that, with the mole fraction of 0–0.45, two dominant pore sizes, i.e. 3.5 nm and 10 nm, are observed. In contrast, when the S/Zr mole fraction is more

than 0.6, the pores with a diameter below 4.0 nm become negligible. It has also been observed that the increase of the S/Zr mole fraction in the range of 0.3 to 0.6 increased the gelling time, which resulted in a decrease of the pore volume [47]. De la Rosa et al. [48] received zirconium oxide (IV) doped with 0.5 wt%. La, Mn and Fe based on the sol-gel method. They analyzed the influence of the type of metallic precursor on the crystalline phase. The authors used zirconium alkoxide and precursors in the form of a metal acetate as substrates. The resulting products were characterized by a surface area in the range of 1.5 to 5.0 m^2/g and a pore size from 5 to approx. 60 nm. It has been shown that the zirconia doping with lanthanum and manganese promotes the formation of the monoclinic phase, and the dopant lanthanum-iron results in the formation of the tetragonal phase of ZrO_2. The resulting products were used in the catalytic combustion of trichlorethylene, so their thermal characteristics were carried out. The authors found an approximately 20% loss of mass when the gelation temperature was 80–200°C. This weight loss may be associated with the evaporation of physically absorbed water and ethanol from the solids. The second weight loss was observed at 200–380°C, which was explained as being the result of the alkoxy group oxidation [48]. The effect of the addition of the precursor metal on the zirconium dioxide crystal structure was also studied by Miyoshi et al. [66]. The authors demonstrated that even a small addition of yttrium (1 mol%) stabilizes the tetragonal phase. The effect of increasing the concentration of yttrium is the creation of equilibrium shares of monoclinic and tetragonal phases. The authors observed this effect in $Zr_{0.96}Y_{0.04}O_{1.98}$. This share phase change with increasing heat treatment temperature to the disadvantage of the monoclinic phase – in 1273 K the amount of this phase is negligible. For $Zr_{0.84}Y_{0.16}O_{1.92}$ both before and after heat treatment, the dominant phase in the crystal was a cubic phase [66].

The sol-gel method is an effective method for obtaining thin layers of ceramic. This has been proven in many publications [44, 45, 67, 68], but also by a combination of hydrothermal methods leading to the acquisition of nanocrystalline powders [32, 36].

3.4. Synthesis of nano-zirconia by microemulsion method

The microemulsion method has already been successfully applied for the preparation of nanoparticles by Boutonnet and co-workers [69] in 1982. The synthesis products by this technique have a uniform size distribution and dispersion. The essence of the method involves mixing together two microemulsions, where there are various reagents in the drops. Then, as a result of mixing, the emulsion liquid droplets collide and exchange reagents. The step of nucleation and crystal growth of product occurs within the droplets and is limited by their diameter (average diameter = 50 nm). In further steps, the reactions of the precipitation and calcination take place. A microemulsion is thermodynamically stable, isotropic and transparent dispersion, which consists of two mutually immiscible liquids – water and oil [51]. The third component of the emulsion is an emulsifier, which is introduced in the form of one or two surfactants with the assumption that the quantity does not exceed 10–15 mass%. of the entire system weight [56]. Into microemulsion, the addition of a co-surfactant is introduced. It prevents the so-called phenomenon of "Ostwald ripening". It occurs when the

monomer particles leak from small droplets of the dispersed phase into large particles through the continuous phase [56]. There are two main types of microemulsion – oil in water microemulsion (o/w) and water-in-oil (w/o) [55]. Most of the examples of zirconia nanoparticle synthesis using the microemulsion technique takes place in a water-in-oil system [53, 54, 70], but there are also known synthesis methods in an oil-in-water system, which are gaining in importance due to the possibility of the use of anionic surfactants [50, 52]. In the o/w microemulsion metal precursors and the precipitating agent are dissolved in the continuous phase, while in the w/o microemulsion, they are inside the droplets of the dispersed phase. Therefore, in the technique based on o/w microemulsion, the synthesis process is different. In a first step, a microemulsion is formed, and then metal cations, which will be adsorbed at the oil-water interface, are added. This is caused by Coulomb forces – the attraction between the metal cation and surfactant anion. The fact that the ions are strongly solvated in polar solvents is also not without significance. As a result, the cation is positioned at the oil-water interface, because it is stabilized by both water and surfactants molecules. After adding the flocculation agent to the system, the equilibrium is destroyed and consequently, at the interface, plurality of product particles are formed [52]. In the w/o microemulsions, the size and shape of the products depend largely on the used surfactant [37, 41, 42, 70], which is shown in Table 1.

Table 1. Examples of the zirconium dioxide synthesis using w/o microemulsion

Microemulsion components			Particle size (diameter) [nm]	Characteristics	Lit.
Oil phase	Water phase	Surfactant			
Heptane and cyclohexane	solution of zirconium salt	Span 80 + Arlacel 83 + isopropanol	$2 \cdot 10^3 - 8 \cdot 10^3$	spherical shape	71,72
Xylene	solution of zirconium and yttrium nitrate	Tween 80	$0,3 \cdot 10^3 - 1,0 \cdot 10^3$	fusiform and spherical shape	73
Cyclohexane	solution of zirconium salt	Triton X –100/ pentanol	4–20	fusiform shape and monoclinic	70
Cyclohexane	solution of zirconium salt	Triton X – 100/ hexyl alcohol	30–40	spherical shape	70
n-Octan	$ZrOCl_2$ solution	Span 80/Triton X-100/n-hexyl alcohol	7.2–23.7	spherical shape	53

The microemulsion method is a versatile technique for the synthesis of nanoparticles, which allows to control properties, such as size, geometry, morphology, homogeneity and surface [50]; therefore, it is regarded as one of the best synthesis methods. In addition, its application does not require the use of expensive and complicated laboratory equipment.

4. Conclusions

Nano-sized zirconia may be obtained from all phases of matter, ie. from the gas and the liquid phase as well as the solid. Methods for obtaining it are chosen based on the chemical synthesis or physical processes. This article discusses some methods for the synthesis of nano-zirconium dioxide from the liquid phase, focusing on the co-precipitation method, hydrothermal methods, sol-gel method and the microemulsion method. All of these methods have advantages and disadvantages. A great advantage of most of them is the lack of the need to use expensive and complicated laboratory equipment, the only exception being the hydrothermal method. Most liquid methods do not require high processing temperatures, unlike the gas phase synthesis methods. Products can be obtained both in the form of powders as well as layers deposited on the substrate. The big advantage is the ability to conduct modification of the final structure of the material, e.g. by applying suitable metal precursors and by carrying out the synthesis under appropriate conditions and in the presence of certain chemicals, e.g. surfactants. Thus, there are several ways to modify the methods of nanometric zirconia synthesis. Based on the cited literature, certain trends of the methods discussed can be seen as well. Hydrothermal methods are supported by the action of microwave energy and ultrasound. It also seems that, in the near future, interest in polymers, substances limiting the agglomeration of particles in aqueous solutions, will increase. Previously quoted example – PEG 800, which did not just cause a limit of the size of zirconium oxide particles, can provide a stimulus to explore this issue. The use, instead of water, volatile organic solvents, having a lower polarity than water, is also a direction of development of nano compound synthesis methods. We cannot determine which method of synthesis is the best because, when considering this issue, the following should be taken into account: access to equipment and chemical reagents, any financial outlay and predispositions as well as skills of people involved in the synthesis. The choice of synthesis methods can also be determined by the type of final material, e.g. powder or layered material.

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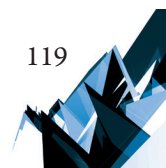
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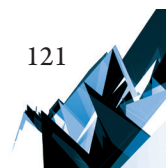
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