Heterophase synthesis of zirconium hydroxides

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Abstract

Zirconium hydroxide is a precursor of nanostructured zirconium oxides (including low-temperature metastable tetragonal ZrO_2) used in the production of catalysts and their carriers, luminophores, ceramics, etc. Despite the variety of areas of application of materials based on zirconium dioxide, powders must have certain characteristics, in particular, a high specific surface area, a given phase composition, morphologies, etc.

Most often, zirconium hydroxide is obtained by precipitation from aqueous solutions of salts with solutions of bases, in this case, gel-like, highly hydrated, and therefore poorly filtered and washed out of impurities, sediments are formed. Differences in the nature and concentration of reagents, precipitation conditions lead to the irreproducibility of the composition of the hydroxide and the oxide obtained from it.

Therefore, in industrial practice, instead of precipitating zirconium hydroxide from solutions of potassium hexafluorozirconate (a semi-product of zircon processing, used in the transition from the crystallization version of the separation technology of zirconium and hafnium to the extraction one), at the Chepetsky Mechanical Plant (CMP) uses the method of heterophase conversion (HC), based on the processing of solid zirconium salt with a base solution, which makes it possible to obtain a low-hydrous hydroxide with a high zirconium content. Such hydroxide ages more slowly, retains its ability to dissolve in acids longer, and has ion-exchange properties.

Heterophase conversion (HC) is an effective method for the synthesis of zirconium hydroxide and from another widely used zirconium compound - zirconium oxychloride, the true composition of which corresponds to the formula $[Zr_4(OH)_8(H_2O)_{16}]\cdot Cl_8\cdot 12H_2O$ or abbreviated $ZrOCl_2\cdot 8H_2O$. Along with octahydrate, crystalline hydrates with a smaller amount of water.

Despite the obvious advantages of the method, there is no information on the kinetic regularities of the conversion process of fluorine- and chlorine-containing zirconium compounds, in particular, fluorozirconates of alkali elements and ammonium.

The purpose of this work: using physical and physicochemical research methods to establish the influence of the conditions of heterophase conversion of fluorine- and chlorine-containing zirconium compounds, which are important for the

technology of separation and purification of zirconium from impurities, on the degree of their conversion into crystal-like zirconium hydroxide, its characteristics (composition, morphology, specific surface, etc.) and thermoevolution into ZrO_2.

To achieve this goal, it is necessary to solve the following tasks:

- to synthesize fluorine and chlorine-containing zirconium compounds of a given composition and morphology;
- to establish the influence of the composition of the halogen-containing precursor, the nature, concentration and temperature of the base, the ratio of reagents on the degree of conversion of zirconium compounds to hydroxide;
- to determine the chemical and phase composition of the synthesized zirconium hydroxides;
- to study the thermoevolution of X-ray amorphous hydroxide at different temperatures;
- to study the products of heterophase conversion and the products of their heat treatment by physical and chemical methods (X-ray phase analysis, scanning electron scanning microscopy, differential thermal analysis, etc.);
- to establish the modes of heterophase conversion, providing the synthesis of crystal-like nanostructured zirconium hydroxide (γ- or δ-form), the heat treatment of which leads to the production of metastable t-ZrO_2.

<u>Scientific novelty of the work:</u>

1. The influence of the conditions of heterophase conversion (HC) of fluorine- and chlorine-containing zirconium compounds on the synthesis of zirconium hydroxide, as well as the temperature of heat treatment on the phase composition and characteristics of the products of thermoevolution, has been studied. It is shown that the phase composition of zirconium oxide is mainly determined by the temperature of the heterophase conversion (HC) process and the temperature of the thermal treatment of the hydroxide.
2. The effect of the composition of fluorozirconate on its heterophase conversion (HC) into crystal-like zirconium hydroxide was studied for the first time. It was found that under comparable conditions the degree of conversion to zirconium hydroxide depends on the ionic radius of the fluorozirconate cation and increases in the series $K^+ < NH_4^+ < Cs^+$. The synthesized hydroxide from hexafluorozirconates is close in composition to the δ-form ($ZrO_{1.5}(OH)$), and from heptafluorozirconates it is a mixture of γ- ($ZrO(OH)_2$) and δ-form. It is shown that the crystal-like hydroxide inherits the morphology of the precursor crystals.
3. The effect of the nature, concentration, temperature of the base, as well as the ratio of reagents on the kinetics of heterophase conversion of K_2ZrF_6 to

zirconium hydroxide was studied. It is shown that the heterophase conversion (HC) process proceeds in the diffusion region. The rate constants were calculated using the Zhuravlev-Lesokhin-Tempelman equation, varying from $1.3\ 10^{-3}$ to $4.3\ 10^{-1}$ min^{-1}, depending on the conditions of the heterophase conversion (HC), and the activation energy of the process (50.1 kJ/mol).

4. The effect of concentration, amount and temperature of a base solution (ammonia, NaOH, KOH) on the process of heterophase conversion (HC) of crystalline hydrates of zirconium oxychloride of different composition into zirconium hydroxide, as well as on its composition and characteristics, has been studied. It was found that the transition of zirconium hydroxide from a gel-like to a crystal-like state occurs in the base concentration range of 0.4-0.6 mol/l, while the hydroxide composition changes from α- ($Zr(OH)_4$) to β-form ($ZrO_{0.5}(OH)_3$), and in more concentrated solutions - to the γ-form ($ZrO(OH)_2$).

Practical significance of the work

The modes of heterophase conversion (HC) of fluorine- and chlorine-containing zirconium compounds, which are important for the technology of separation and purification of zirconium from impurities, have been established, ensuring the production of crystal-like nanostructured zirconium hydroxide of a given composition with a specific surface area of 170-250 m^2/ g, heat treatment of which at a temperature of ≤700°C leads to metastable t-ZrO_2 with crystallite size less than 20 nm. The obtained results can be used in zirconium technology to create new and improve existing technological schemes for the production of hydroxide and zirconium dioxide used to create ceramic materials, sorbents, catalysts or catalyst carriers, and other functional materials.