TITANIA SOLS AS PRECURSORS OF COMPOSITE MATERIALS FOR PHOTOCATALYSIS, ELECTRORHEOLOGY, SORPTION

A. Murashkevich, O. Alisienok, I. Zharskiy, M. Novitskaya, e-mail: alisiyonak@belstu.by Belarusian State Technological University (Minsk, Republic of Belarus)

By changing the nature of initial components, the ratio of precursors, the heat treatment modes and using modifying and structuring components different in their nature, it is possible not only to control the textural characteristics of the obtained nanodisperse composites efficiently, but also to tune a phase composition, which also allows controlling their functional properties: photocatalytic, sorption, electrorheological.

Preparation of TiO_2 sol involved precipitation of hydrated titania from an aqueous solution of titanium tetrachloride by an ammonium carbonate solution followed by peptization of the precipitate in the presence of acid. The effect of precipitation temperature and pH on the phase composition of the obtained product and filtration rate, as well as influence of the nature of acid peptizator on sol formation rate and stable state duration were studied.

The particle size of titanium dioxide hydrosols less than 30 nm is maintained for 100–400 h (depending on the concentration of the solid phase and the acid-peptizer type). In this regard, as-prepared titania hydrosols are preferred to be used, but it is also possible to restore them from naturally dried xerogels (repeptization) that have the ability to peptize in water without introducing additional components. A feature of such xerogels is a significant increase in the size of the particles of the repeptized hydrosol. However, synthesis of hydrated titania at elevated temperatures (30–70°C) significantly suppresses the sol particles' tendency to grow, probably due to a higher degree of titania crystallization; and, as a result, its lower tendency to form aggregates in the process of drying. Hydrosols prepared from precipitates obtained at 70°C slightly change the size after repeptization in water. Photocatalytic activity of the "SiO₂ core – TiO₂ shell" composites based on such sols increases by1.3 times with an increase in the synthesis temperature from ambientone to 70°C.

The initial "SiO₂ core – TiO₂ shell" composite used as photocatalyst contains silica particles coated with a layer of nanosized titania in the anatase structure (crystallite up to 40 nm). The particle size of the composite is 150–250 nm, while the shell consists of smaller particles of titania. The composite particles form complex aggregates of irregular shape, while maintaining a specific surface of 97– $265m^2/g$, sorption volume up to $0.26 \text{ cm}^3/g$. The isotherm of low-temperature nitrogen adsorption – desorption for the "SiO₂ core – TiO₂ shell" composite is type IV with H3 hysteresis inherent in slit-shaped mesopores. It was shown that an increase in the photocatalytic activity of "SiO₂ core – TiO₂ shell" composite is achieved by introducing ammonium hydroxide (n(NH₄OH)/n(TiO₂) = 0.06–0.37) and treatment at 750–800°C.

When sunlight is used as an activating radiation, the Rhodamine FL-BM decomposition rate constants decrease (approximately y 2 orders of magnitude).

However, the introduction of ammonium hydroxide in the composite allows increasing the photocatalytic activity of the material even under these activation conditions. A significant (up to 2.7 times) increase in the photocatalytic process rate is probably associated with a significant increase in the specific surface of the composite, changes in the density and structure of the aggregates.

The ERD filler was obtained by the sol-gel method, which includes the following stages: mixing the titania sol with solutions of modifiers (aluminum nitrate and phosphoric acid) and a structuring component (ammonium carbonate). At this stage, the sol-gel transition of the main component took place; the obtained gel was dried in a microwave oven, the dried product was ground in a planetary mill and then was calcinated.

There are two possible methods to improve the efficiency of titania as a filler of electrorheological dispersions. The first is to obtain the product in an extremely hydrated form. In this case, the electrorheological effect is activated by various forms of water bounded to the surface of titania particles. The second approach involves introduction of modifying and structuring components in the product preparation process. They must not only provide high dispersion of the product after high-temperature treatment, but also create structural defects efficiently responding to exposure to external electric fields. Therefore, we gave chosen the second method – choosing modifiers and structuring components to activate the electrorheological performance of almost anhydrous fillers.

An important point is the nature and degree of interaction between the main components of composites and modifiers, which affects both volume characteristics and their surface properties that are extremely important in adsorption, catalysis, and electrorheology.

Due to their unique ability to form stable complexes with ions and neutral molecules, crown ethers is widely used in extraction processes, interfacial catalysis, organic synthesis, analytical chemistry, biology, and medicine. To increase the efficiency of physical crown ethers adsorption, a surface enriched with active groups is necessary. As crown ethers substrates, individual oxides of silicon, titanium, aluminum have a number of distinct advantages: high dispersion, mesopore order, thermal stability (less typical of titania), a wide variety of morphological forms: aero-, xero-, and coagels, precipitated powders, mesostructured substances, core/shell structures, nanotubes and some other related nanostructures.

Crown ethers immobilization on a surface of particles of a $SiO_2 - TiO_2$ composite has been shown to be leading to a significant increase in the adsorption capacity of the received organo-mineral composites in relation to a number of cations of metals from acid aqueous solutions.