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PRODUCTION OF TiO_2/Cr_2O_3 COMPOSITE MATERIAL IN THE SPHERICAL FORM

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Abstract

Spherical TiO_2/Cr_2O_3 oxides composites were obtained by template method accompanied with sol–gel method. Ion exchange resins of spherical form (*TOKEM-100* and *TOKEM-250*) were used as an organic polymer matrix. Thermal analysis, X-ray phase analysis and micro-X-ray spectral analysis were used to identify the formation process and compositions of oxides composites. The formation of spherical oxide composite ends at 400 °C and the final products are a mixture of two oxides: Cr_2O_3 and TiO_2 regardless of the structure of the used template. According SEM data prepared TiO_2/Cr_2O_3 composites have spherical form and the size of sphere found to be in a range from 300 to 870 μm

Keywords

Titanium dioxide, chrome (III) oxide, spherical composites, template method, sol-gel method

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Introduction. At current, mixed valence metal oxides used widely in catalysis process [1–4]. Oxide composites based on Cr_2O_3 и TiO_2 are advanced catalysts in the reactions of deep and partial oxidation of hydrocarbons [5], their dehydrogenation [6], and also possess photocatalytic activity [7–9].

Scientists from all over the world pay close attention to the development of catalytically active oxide composites in spherical form. This form of catalyst granules is technologically attractive for several reasons: spherical granules are characterized by high abrasion resistance; they contribute to catalytic units stable operation with moving and fluid beds, easily moving from the reactor through the regeneration section and back into the moving bed, providing a continuous reaction and catalyst regeneration [10]. At current, these catalysts are manufactured by applying a catalytically active substance on a spherical carrier formed by suspensions moulding into granules, for example, catalysts based on alumina carrier [11–14]. As shown in the research [14], one of the most important

problems of granulation is the production of granules with targeted properties. One of the ways to solve this problem is to use template and sol-gel synthesis methods in spherical catalysts manufacturing. Thus, in works [15, 16], was shown to obtain spherical aglomarates, being the TiO_2 layer applied on SiO_2 spheres previously prepared with the sol-gel method using the structure-forming agent (cetyl trimethyl ammonium bromide, CTAB) [17].

The actual task for researchers is to find out alternative methods for obtaining spherical composites with targeted properties, the choice of template, the establishment of optimal parameters that contribute to the materials production with given catalytic properties. Using the example of metal oxide composites of $YBa_2Cu_3O_{7-\delta}$ and $TiO_2–SiO_2$ composites production in works [18–20], it was shown that ion exchange resins could act as a template. Earlier [5, 21], it was indicated that ion exchange resins could be used as a template for the preparation of catalytically active oxide composites $TiO_2–SiO_2/Cr_2O_3$ and $TiO_2–SiO_2/Co_3O_4$ with a spherical shape of aglomerates.

The purpose of the work is to obtain spherical oxide composites of TiO_2/Cr_2O_3 using the method based on sol-gel technology and template synthesis, and to investigate their phase composition and morphology.

Experimental technique. As a template for spherical composites, ion-exchange resins with various natures were used: *TOKEM-100*, *TOKEM-250* (manufactured by *TOKEM PO LLC*, Russian Federation). The ion exchange resin *TOKEM-250* is a polymer with a macroporous structure with an acryl-divinylbenzene matrix containing carboxyl functional groups. The components of the *TOKEM-100* polymer composition have a gel-like structure and contain styrene-divinylbenzene units with sulfo functional groups.

The preparation of spherical granules was done in several stages, which was proposed in works [22]. The first stage was in placing the templates (cation exchange resins *TOKEM-100*, *TOKEM-250*) in a saturated aqueous of chromium(III) nitrate ($Cr(NO_3)_3 \cdot 9H_2O$, pure 99 %, *Yugreaktiv* company) for 6 hours in constant agitating conditions on a magnetic stir bar at room temperature. Then the polymer was dried for 2 hours at 60 °C in air. The second stage is the preparation of an aggregative-stable sols according to the method represented in Ref. [23]. To prepare the sol, tetrabutoxytitanium (TBT, extrapurity, Acros, USA, $Ti(C_4H_9O)_4$ with concentration 0.1 mol/L), distilled water (H_2O with concentration 0.4 mol/L) and nitric acid (pure 99%, *UralPromPostavka LLC*, Russian Federation, HNO_3 with concentration $2.5 \cdot 10^{-3}$ mol/L, using butyl alcohol as a solvent (pure 99%, “EKOS-1” JSC,

Russian Federation). The process of aging of solution took three days after preparation. Ion exchange resins with sorbed chromium(III) ions were placed into the finished sol for 12 hours. The obtained samples were marked as TBT/Cr^{3+}(100), TBT/Cr^{3+}(250), depending on the ion exchange resin used. Then, spherical granules of TBT/Cr^{3+}(100), TBT/Cr^{3+}(250) were dried for 30 minutes at a temperature of 70 °C in a loss-on-drying oven and annealed in a muffle furnace for 30 min at the temperature of 100, 200, 250, 300, 350 °C and 1 hour at a temperature of 400 °C. After heat treatment, the obtained samples were marked as TiO_2/Cr_2O_3(100) and TiO_2/Cr_2O_3(250) respectively.

The processes of oxide systems formation during temperature treatment of samples TBT/Cr^{3+}(100), TBT/Cr^{3+}(250) were examined by means of thermal analysis. The research was done on a synchronous thermal analyzer *STA 449 C Jupiter* (*Netzsch-Gerätebau GmbH*, Germany) in the temperature range of 30–900 °C in air. Sample heating rate was 5 °/min. Heating was done in corundum (Al_2O_3) crucibles.

The phase composition of samples obtained after annealing was determined by X-ray phase analysis (XRD) on a *MiniFlex 600* diffractometer (*Rigaku*, Japan) with CuKα radiation. The shooting was carried out in the range of angles 2θ 10–80°. Identification of the synthesis products was done according to the international data bank PDF-2.

The surface morphology of the obtained oxide composite materials was examined on a *TM-3000* scanning electron microscope (SEM) (Hitachi, Japan) with an accelerating voltage of 15 kV (electron gun $5 \cdot 10^{-2}$ Pa, camera for the sample 30–50 Pa). X-ray microanalysis was performed on the *Shift ED 3000* console using energy dispersive X-ray.

Results and discussion. The most important step in the production of spherical oxide composites by the proposed method based on sol-gel technology and template synthesis is a stepwise temperature treatment of polymer matrices treated with chromium(III) nitrate solution and a tetrabutoxytitanium-based sol. The temperature treatment modes for TBT/Cr^{3+}(100), TBT/Cr^{3+}(250) samples were selected based on the results of the thermal analysis performed: thermogravimetric (TG) and differential scanning calorimetry (DSC) (Fig. 1).

The thermal decomposition of examined samples, despite of the cation exchanger selected as a template, proceeds in three main stages, which is confirmed by the presence of three areas of sample mass alteration on TG curves (Fig. 1, *a*). This process is accompanied with low endothermic effects (Fig. 1, *b*),

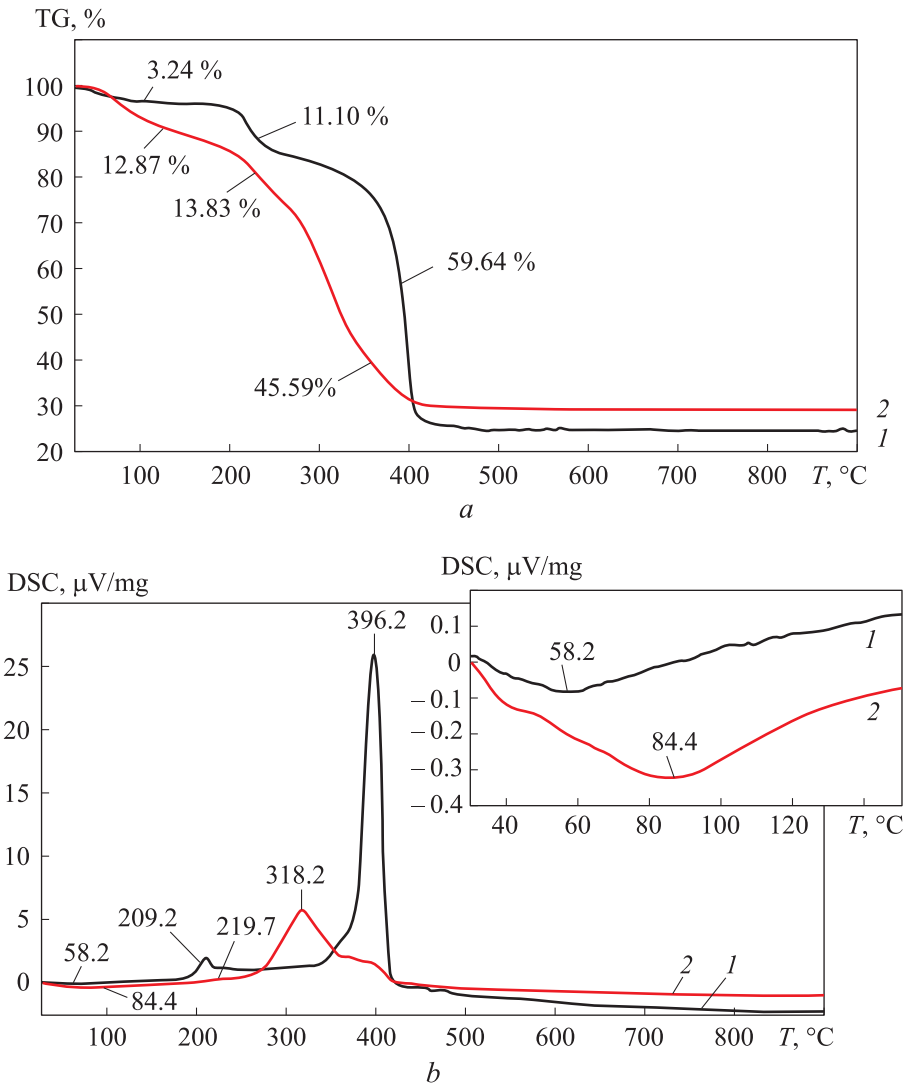

Fig. 1. Thermal analysis results:

a TG-curves for TBT/Cr^{3+}(100) (*1*) and TBT/Cr^{3+}(250) (*2*) samples; *b* DSC-curves for TBT/Cr^{3+}(100) (*1*) and TBT/Cr^{3+}(250) (*2*) samples

which is typical for the process of water desorption from the surface of the samples. Ion exchange resins are wet polymeric materials, their dehydration is complicated by high pore volume, advanced specific surface, content of polar groups and contaminations of metal ions. According to the data of [24, 25], ion-exchange resins, saturated with metal ions, are able to sorb water and retain it in the form of weakly hydrated water due to a weak bond with counter-ions — metal ions. At temperatures of 209.2 and 219.7 °C, small exothermic effects are observed for samples TBT/Cr^{3+}(100) and

TBT/ Cr^{3+}(250) (see Fig. 1, *b*), which can be associated with chemically bound water desorption in the second stage of their decomposition within the temperature range of 85–250 °C. At the third stage, within the range of temperatures of 250–400 °C, the complete thermal destruction of examined samples happens, proceeding with a large heat release, which is associated with thermal destruction of TBT based sol, and to a greater extent with the destruction of ion exchange resins, oxidation and removal of volatile decomposition products. For the TBT/Cr^{3+}(100) sample, exothermic effects are observed at the temperature of 396.2 °C, and for the TBT/Cr^{3+}(250) sample are observed at the temperature of 318.2 °C (see Fig. 1, *b*). According to the TG curves (see Fig. 1, *a*) and the XRD results (Fig. 2), decomposition of the studied samples, regardless of the cationite used structure, is completed at a temperature of approx. 400 °C.

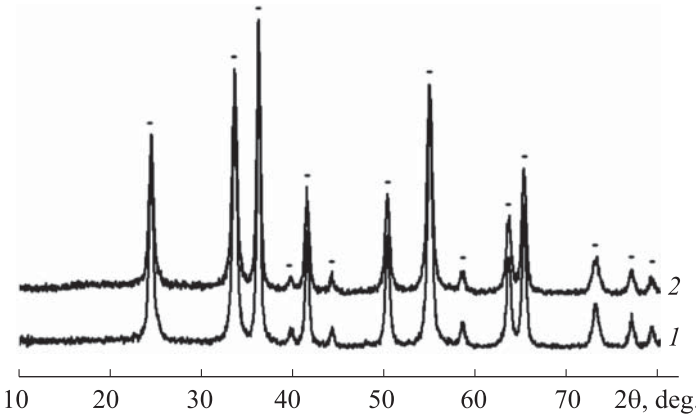

Fig. 2. X-ray pattern of samples TiO_2/Cr_2O_3(100) (*1*) and TiO_2/Cr_2O_3(250) (*2*)

The samples of TiO_2/Cr_2O_3(100) and TiO_2/Cr_2O_3(250) obtained after annealing are Cr_2O_3 with a corundum structure. The X-ray patterns of the examined samples (see Fig. 2) correspond to the data of the crystal peaks of the PDF-2 database (maps no. 00-038-1479), where a = 4.960 Å and c = 13.597 Å (2θ = 24.40; 33.56; 36.16; 39.67; 41.48; 44.17; 50.24; 54.87; 58.38; 63.42; 65.09; 72.90; 76.74; 79.02). The dimensions of the coherent scattering areas are 16.8 nm (sample TiO_2/Cr_2O_3(100)) and 18.4 nm (sample TiO_2/Cr_2O_3(250)). Reflexes corresponding to the TiO_2 phase were not indicated on any of X-ray patterns, which could be due to the fact that the amount of titanium dioxide formed is below the detection limit of this method (less than 5 wt. %).

The presence of the titanium phase in the obtained spherical composites is confirmed by the results of the qualitative (Fig. 3) and quantitative micro-X-ray

spectral analysis. The results of quantitative X-ray microanalysis show that the content of the titanium compound in the samples is less than 4 wt. %, which correspond with the XRD data.

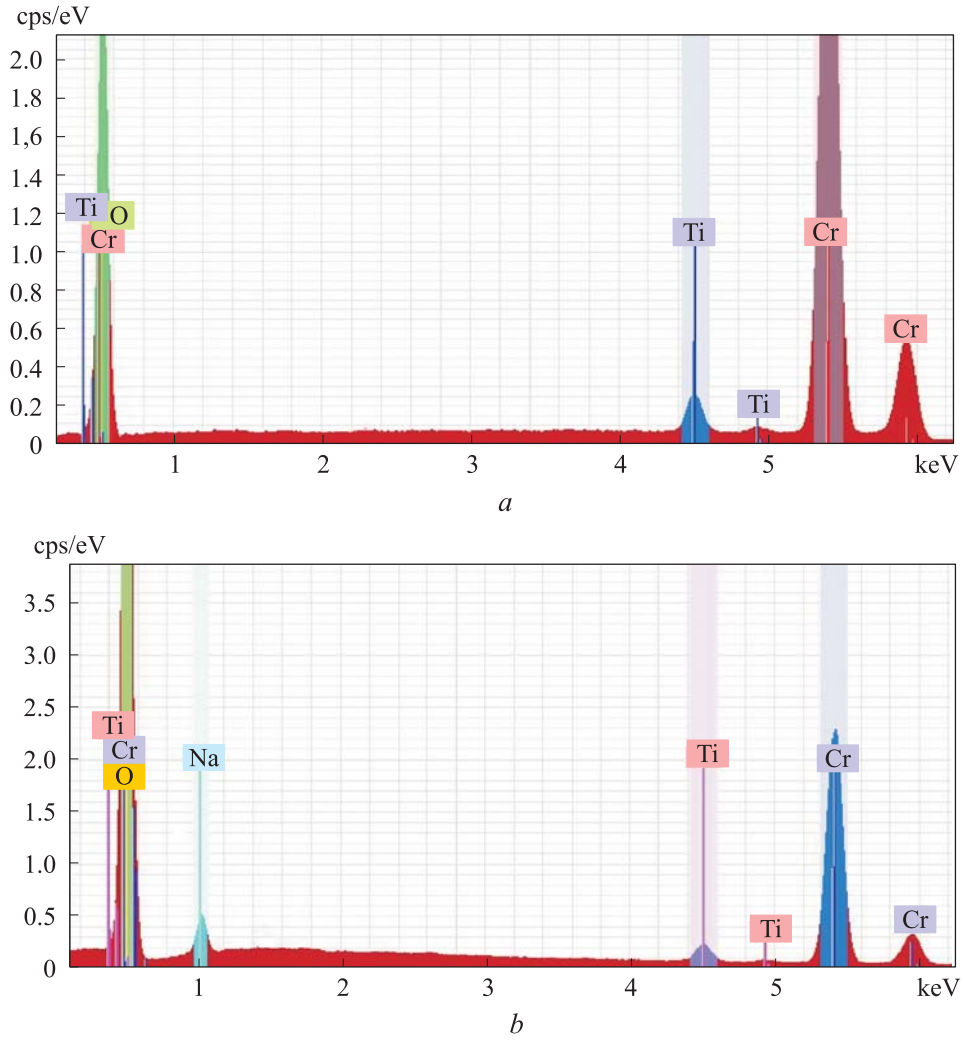

Fig. 3. Results of X-ray microanalysis of samples: TiO_2/Cr_2O_3(100) (*a*) and TiO_2/Cr_2O_3(250) (*b*)

The spectrum of both samples contains emission lines specific for chromium (at 0.5, 5.4, and 5.9 keV), titanium (at 0.39, 4.5, and 4.9 eV) and oxygen (at 0.6 keV). The spectrum of the sample TiO_2/Cr_2O_3(250) also contains a spectral line at 1.1 keV, specific for sodium. This may be due to the fact that the TOKEM-250 cation exchanger used as an organic matrix was used in sodium form and as a result of sorption, not all sodium ions were replaced

by chromium (III) ions. According to researches of such systems [5, 21, 23] and based on XRD data and micro-X-ray spectral analysis, we assume that the samples obtained are oxides TiO_2 and Cr_2O_3.

SEM data indicated that $TiO_2/Cr_2O_3(100)$ and $TiO_2/Cr_2O_3(250)$ (Fig. 4, *a*, *c*) samples have a spherical form. The size of the spheres of all samples presented lies in the range of values of 300–870 μm.

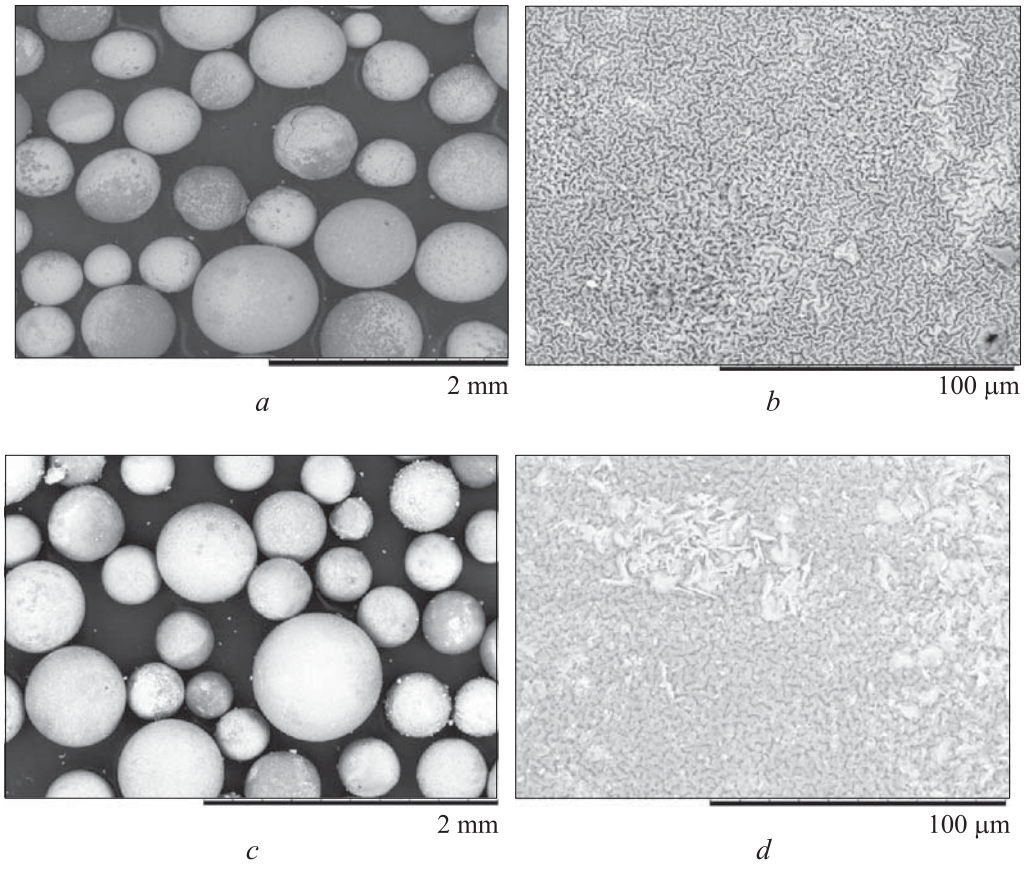

Fig. 4. SEM image of samples: $TiO_2/Cr_2O_3(100)$ (*a*, *b*) and $TiO_2/Cr_2O_3(250)$ (*c*, *d*)

The surface morphology of the $TiO_2/Cr_2O_3(100)$, $TiO_2/Cr_2O_3(250)$ sample spheres is a relief (Fig. 4, *b*, *d*), consisting of herringbone convexes and dimples distributed over the entire surface of a spherical granule. On separate parts of the surface, larger clusters of oxide crystals are formed, closely adjacent to each other.

Conclusion. Spherical shape TiO_2/Cr_2O_3 oxide composites were obtained with the method based on sol-gel technology and template synthesis, using ion-exchange resins with various structures as templates. It is found out that staged

heat treatment leads to the decomposition of cation exchangers and synthesis precursors with the formation of oxide composites that retain the spherical shape of the template. Despite the structure of used ion-exchange resin, the formation of TiO_2/Cr_2O_3 oxide composites is completed at the temperature of 400 °C and obtained samples have a similar surface morphology of spherical granules. The resulting spherical composites TiO_2/Cr_2O_3(100) and TiO_2/Cr_2O_3(250) could be used as catalysts in hydrocarbons oxidation.

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