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EVALUATION TEMPLATES ACTING ON NANOPARTICLES

Purpose. *Investigation of the influence of templates on nanoparticle size of cerium dioxide.*

Methodology. *Cerium dioxide nanoparticles are obtained on carbon, aluminum silicates, nanotubes, kaolin and in solution by chemical precipitation from solutions of cerium salts in an alkaline medium.* *The particle size of cerium oxide was determined by transmission electron microscopy.*

Results. *Cerium dioxide nanoparticles are obtained on carbon and halloysite nanotubes, kaolin and in solution by sol-gel method.*

Scientific novelty. *A method is proposed for quantitative comparison of the structure-forming effect of templates on particle size under identical conditions for their synthesis.*

Practical value. *It was shown that with the use of organic templates and ultrasonic treatment during the synthesis, it is possible to reduce the nanoparticle size.*

Keywords: *synthesis, templates, nanonanotubes, kaolin, cerium oxide, particle size.*

Introduction. Nanoscale tubes, due to their morphology, are attractive as carriers for the synthesis of nanoparticles on their surfaces and in cavities in order to create demanded materials with the necessary physical and chemical properties [1, 2]. For example, carbon and aluminum silicates (halloysite) nanotubes successfully counteract corrosion due to the physical barrier to the aggressive agents they create. The cerium compounds have an anticorrosive protection of metals by the cathode mechanism. The composites synthesized by us, containing nanotubes and cerium oxide, showed a synergy in the anticorrosive action. These materials, according to X-ray phase analysis data, contain cerium dioxide of a cubic structure. The rate of release of biologically active molecules and other compounds adsorbed on nanotubes in solution is 50-100 times lower than for micro- and nanoparticles of other carriers. We have developed composite silicate materials, carbon nanotubes/cerium oxide for use in oxidation-reduction catalysis and other fields [3, 4].

During the work on applying modifiers and establishing the properties of materials, the task was to quantitatively compare the effect of the nature of the templates (carriers) on the particle size of the cerium oxide. The aim of the publication is to establish the quantitative regularities of the formation of cerium dioxide on carbon and halloysite nanotubes, kaolin and in solution under identical synthesis conditions.

Objectives. The syntheses used catalytic multilayer carbon nanotubes (Nanothinx S.A.) with diameters of 12-31 nm of 97% purity (about 2% is iron-containing catalyst and less than 1% pyrolytic carbon), halloysite nanotubes (NaturalNano, Inc.) with diameters of 25-50 nm 88-95% purity and kaolin (P-2 "Disten Limited"). Templates (carriers) were modified by precipitation of cerium oxide from solutions of salts in an alkaline medium. The synthesis of cerium oxide without templates was also carried out.

The synthesis conditions for obtaining samples with 5% cerium oxide content were given identical (automated reactor "Syrris"): the temperature of the reaction mixture was 23 °C, the weight of the template carrier (50 g), the constant stirring speed of the reaction mixture throughout the synthesis process 1200 rpm), the rate of addition of reagent solutions and their concentrations (1M $Ce(NO_3)_3$, 50 ml/min, 2M NH_4OH, 5 ml/min). The time of each synthesis was determined by the achievement of pH=8.5. The resulting precipitate of cerium composites or cerium oxide was filtered off and dried at 120 °C.

According to atomic emission spectrometry (ICPE-9000, Shimadzu), cerium content in the samples in terms of dioxide is 4.37±1.335 (carbon nanotubes of CNT/CeO_2), 4.96±0.025 (silicate nanotubes of GNT/CeO_2), 4.85±0.015 (kaolin of Kaol/CeO_2) and 5.06±0.005% (solution Solut/CeO_2), the uncertainty value of the confidence interval is given. In reproducible syntheses, the underestimated results of the content of cerium oxide are probably primarily explained by the effect of the filtration step in the synthesis process. The samples were characterized with a Hitachi H-800 transmission electron microscope (TEM) using the electron diffraction method in the selected region. The particle size was determined on TEM images in a dark field using a linear measurement program and sampling more than 100 particles for each sample. The UV spectra of the powders were recorded on a UV-VIS-NIR spectrophotometer UV-3600, Shimadzu in the reflection mode in the 220-800 nm range with an instrument uncertainty of ±1 nm.

Research results. Usually, in order to obtain nanoscale inorganic particles, the conditions for the synthesis are carefully chosen: the concentration of the reagents, the rate of addition and mixing of the components, the pH of the medium, the temperature, and the template. Effective action of organic and inorganic templates is due to two factors - chemical (surface nature, the ability to form chemical and hydrogen bonds, the formation of intermediates, etc.) and physical (size, morphology, aggregation ability, thermal conductivity, etc.). Our experience suggests that cerium dioxide in the nanoscale can be produced in a wide range of concentrations up to 20% using nanosized oxide carriers from dilute solutions [5].

TEM images of synthesized materials in light and dark fields provide reliable information on the particle size of the oxide. In the materials on the carriers, the modifier particles are observed to be much smaller in size, different morphology than the particles of carriers and impurities. The differences between pure carriers and modified ones are especially noticeable in TEM images in a dark field. Electron diffraction studies of modifying particles in the samples revealed reflexes d(hkl)=3.12(100), 2.7(200), 1.89(220), and 1.64 Å (311), which identify the cubic structure of cerium dioxide. X-ray diffraction analysis also confirmed the formation of crystalline cerium dioxide during the synthesis. Significant blurring of the modifier signals can be explained by the size effect and the low degree of crystallinity of cerium dioxide. The particle size of cerium dioxide for the samples ranges from 1-7.8 nm for CNT/CeO_2, 2-14.5 for GNT/CeO_2 and 3.9-19.8 nm for Kaol/CeO_2. The maximum particle size distribution of cerium oxide is 2.4, 4.8 and 7.6 nm, respectively. We estimated the error in determining the dimensions by about 5-7% for the mean diameter and 10-15% for the maximum distribution. The choice of particles in the images was carried out in homogeneous regions without visible regions of aggregation. Obviously, in the series of kaolin, halloysite, and carbon nanotubes, the effect of the carrier effect on the unit of mass contributing to the formation of particles with a smaller diameter is observed. The particle size of CeO_2 synthesized without carriers was 3.5-16.8 nm. It lies between the dimensions of the oxide particles on the GNT and kaolin. Consequently, nanotubes contribute to a decrease in the size of the synthesized particles - a positive templating action, and kaolin to increase - a negative templating action.

The quantitative evaluation of the structure-forming action of β can be expressed as a function of the effect of the template during the synthesis on the size of the particles of the same type $\beta=(d_s-d_t)/d_s\cdot100\%$, where d_s is the average particle diameter that is formed without the template carrier, d_t is the average particle diameter, formed under the influence of the template. This estimate is valid for the same series of syntheses under identical conditions. The templating influence is suggested to calculate the maximum particle size distribution for the size $\beta_m=(d_{ms}-d_{mt})/d_{ms}\cdot100\%$, where d_{ms} is the maximum particle distribution that is formed without the template carrier, d_{mt} is the maximum distribution of the particles formed under the effect of the template. Obviously, the accuracy of determining the average particle diameter and the maximum diameter distribution will be different. Carbon nanotubes, according to the calculation of the templating action, have the greatest positive effect on the size of the synthesized cerium oxide (Table). The structural-forming effect of CNT on the average diameter was 49.3%, with a maximum distribution of 53.8%. The difference in the value is within the measurement error. Kaolin, on the contrary, contributes to the formation of particles of large sizes, so the values of β and β_m have a negative sign -19.4 and -46.2%.

With the use of organic templates and ultrasonic treatment during the synthesis, it is possible to reduce the particle size by a factor of two, and the effect of ultrasound and other factors can also be described quantitatively by the method proposed above [6].

Table 1

Calculation of the structure-forming effect of the templates on the particle size of cerium dioxide at d_s=6.7 and d_{ms}=5.2 nm

Samples	Average particle diameter d_t, nm	Maximum particle size distribution d_{mt}, nm	The structure-forming effect on the average diameter β, %	The structure-forming effect on the maximum of the distribution of $β_m$, %
CNT/CeO_2	3,4	2,4	49,3	53,8
GNT/CeO_2	6,3	4,8	6,0	7,7
Kaol/CeO_2	8,0	7,6	-19,4	-46,2

In macro- and microcrystalline samples, tetravalent cerium in the UV region gives a signal of about 400 nm, which corresponds to the transition of the charge O^{2-}(2p)→Ce^{4+}(4f). The signal overlaps with an electronic transition of 5d1→4f1 Ce^{3+} ions. Usually, defects in the form of trivalent cerium are fixed in the structure of cerium dioxide, the appearance of which is due to the low energy of the Ce^{3+}↔Ce^{4+} transition. During the synthetic procedure, the oxidation of cerium (III) hydroxide probably does not occur until the end, and the Ce^{4+}→Ce^{3+} reaction also takes place upon contact with the reducing agents. Ce^{3+} ions are embedded in the crystal structure of cerium dioxide instead of Ce^{4+} as a defect and the spectral transition O^{2-}(2p)→Ce^{3+}(4f) is observed about 250 nm [7]. A number of functional properties of cerium dioxide, including physiological, is determined by the size factor and the Ce^{4+}/Ce^{3+} ratio. The UV spectra of nanocomposite samples with cerium dioxide nanoparticles revealed maxima at 370-420 nm and 260-290 nm. In this case, the templates have their own signals in the UV region, which makes interpretation of the spectra difficult and an analysis of the ratio of tri- and tetravalent cerium depending on the particle size of cerium dioxide.

Conclusion. Cerium dioxide nanoparticles are obtained on carbon and halloysite nanotubes, kaolin and in solution by sol-gel method. The particle size of the modifier was determined by the transmission electron microscopy method. Electron diffraction studies have established that the modifiers are cerium dioxide particles of a cubic structure. A method is proposed for quantitative comparison of the effect of templates on particle size under identical conditions for their synthesis.

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ВИЗНАЧЕННЯ СТРУКТУРОФОРМУЮЧОЇ ДІЇ ТЕМПЛАТІВ НА СИНТЕЗ НАНОЧАСТОК

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Мета. *Дослідження впливу темплатів на розмір наночастинок діоксиду церію.*

Методика. *Наночастки оксиду церію одержані на вугіллі, силікаті алюмінію, нанотрубках, каоліні і в розчині методом хімічного осадження з розчинів солей церію в лужному середовищі. Розмір частинок оксиду церію визначали методом трансмісійної електронної мікроскопії.*

Результати. *Отримані наночастинки оксиду церію на вуглецевих і галоізитних нанотрубках, каоліні та в розчині з використанням золь-гель методу.*

Наукова новизна. *Запропоновано метод кількісного порівняння структуроформуючої дії темплатів на розмір часток при ідентичних умовах їх синтезу.*

Практична значимость. *Показано, що шляхом використання органічних темплатів і ультразвукової обробки в процесі синтезу можна зменшувати розмір наночасток.*

Ключові слова: *синтез, темплат, нанотрубки, каолін, оксид церію, розмір часток.*

ОПРЕДЕЛЕНИЕ СТРУКТУРОФОРМИРУЮЩЕГО ДЕЙСТВИЯ ТЕМПЛАТОВ НА СИНТЕЗ НАНОЧАСТИЦ

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Цель. *Исследование влияния темплатов на размер наночастиц двуокиси церия.*

Методика. *Наночастицы оксида церия полученны на угле, силикате алюминия, нанотрубках, каолине и в растворе методом химического осаждения из растворов солей церия в щелочной среде. Размер частиц оксида церия определяли методом трансмиссионной электронной микроскопии.*

Результаты. *Полученны наночастицы оксида церия на углеродных и галоизитных нанотрубках, каолин и в растворе с использованием золь-гель метода*

Научная новизна. *Предложен метод количественного сравнения структуроформирующего действия темплатов на размер частиц при идентичных условиях их синтеза.*

Практическая значимость. *Показано, что путем использования органических темплатов и ультразвуковой обработки в процессе синтеза можно уменьшать размер наночастиц*

Ключевые слова: *синтез, темплат, нанотрубки, каолин, оксид церия, размер частиц.*