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Synthesis and characterization of thermally stable large-pore mesoporous nanocrystalline anatase

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ABSTRACT

Thermally stable mesoporous nanocrystalline TiO_2 with a pure anatase structure was obtained by sol–gel synthesis (in combination with hydrothermal treatment) using titanium tetrabutoxide and dibenzo-18-crown-6 as a structure-directing agent in presence of surfactant and/or La^{3+} ions additives. Nanocrystalline TiO_2 demonstrates various textures with a well-defined spherical morphology (micro- and nanospheres), a crystallite size of no greater than 10 nm (XRD), and a narrow pore size distribution. Spherical particles of micrometer scale in the presence of La^{3+} ions do not form. TiO_2 calcined (at 500 °C) after hydrothermal treatment (at 175 °C) has a significantly more developed porous structure as compared with TiO_2 which was not treated hydrothermally. For example, specific surface area amounts 137 $m^2\,g^{-1}$ and 69 $m^2\,g^{-1}$, pore volume 0.98 $cm^3\,g^{-1}$ and 0.21 $cm^3\,g^{-1}$, pore diameter 17.5 nm and 12.5 nm respectively for samples hydrothermally treated and not treated.

1. Introduction

Titanium dioxide is a high demand oxide, widely used in different fields of industry, medicine, and biology [1–10]. During the last 20 years titanium dioxide as an adsorbent having semiconducting properties with a band gap of 3.2 eV has attracted considerable interest as one of the most promising photocatalysts. Vast numbers of redox transformations of both inorganic and organic substrates may occur on the surface of titanium dioxide including water decomposition with hydrogen and oxygen generation and oxidation of harmful organic compounds to carbon dioxide and water. These properties of titanium dioxide can make a significant contribution towards the solving of energetic and ecological problems of modern society [2,6–10]. Effective TiO_2-photocatalyst should possess a certain set of parameters, such as phase constitution, degree of crystallinity, crystallite size, surface organization, developed specific surface area, porosity, etc. Following Brinker and Scherer, "the ideal powder should be pure, stoichiometric, dense, spheroidal, and nearly monodisperse" [11].

Sol–gel synthesis is one of the most widely used methods for the preparation of mesoporous metal oxides [1,2,4,6,12–46]. By introducing various additives, the method allows one to obtain monodisperse particles with controllable pore size and volume in the nanometer range as well as regulating the interactions between particles at a certain stage of formation of the inorganic framework that is a necessary condition for the formation of materials with a defined texture. In 1995 Antonelli and Ying [12] showed broad perspectives for the synthesis of mesoporous TiO_2 by offering their modified variant of the sol–gel method. For the first time, they synthesized mesoporous TiO_2 with a high specific surface area using phosphorus-containing surfactants as templates.

There are two problems to be solved in the preparation of mesoporous TiO_2 with high photocatalytic activity: (1) to remove the template completely, and (2) to carry out the crystallization of TiO_2 via calcination, preventing the total destruction of the mesopores due to the extensive growth of crystallites. As anatase has the highest photocatalytic activity among the three main crystalline modifications of TiO_2, it is clear that the vast majority of research is focused at synthesizing active photocatalysts consisting of mesoporous TiO_2 with nanosized anatase walls. As a rule, amphiphilic poly(alkylene oxide) block copolymers and various surfactants are used as structure-directing agents for the formation of mesoporous structures [1,2,6,12–35]. It is

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known, that alkylene oxide segments of amphiphilic block copolymers can form crown ether type complexes with many metal ions through weak coordination bonds [14,21].

In the context of the choice of a proper template, one undoubtedly is interested in the synthesis of zeolite, EMT [47–49]. EMT was first obtained by Delprato et al. [47] using crown ether in the form of $[\text{Na-18-crown-6}]^+$ complex as a template playing a key structure-directing role during the crystallization of zeolite. Franco et al. [50] found that crystallization of zeolite SAPO-5 in a hexane-aqueous system in the presence of a cationic surfactant leads to profound changes in the crystal morphology. Later Sun et al. [49] proposed a novel route for EMT synthesis. The small addition of various surfactants considerably changed the properties of traditional reaction mixture that allowed obtaining zeolite with a smaller particle size. Such zeolite showed higher catalytic activity in the alkylation of isobutene with butenes. To increase the thermal stability and photocatalytic activity of mesostructured materials, a doping with small amounts of rare-earth cations—Ce^{3+} and La^{3+} was successfully used [15,51–54].

Previously, we have demonstrated [55] the possibility of obtaining mesoporous nano-sized TiO_2 (meso-nc-TiO_2) by the sol–gel method combined with hydrothermal treatment (HTT) using tetrabutoxide titanium (TBOT) as the titanium source and dibenzo-18-crown-6 (in the form of [Na(DB18C6)]Cl complex, due to the low solubility of the crown ether in butanol (BuOH)), as a template. It has been shown [56] that the addition of small amounts of cationic surfactant dodecyldimethylethyl ammonium bromide (DDMEABr) to the reaction mixture leads to an increase in crystallinity and modification of the texture of meso-nc-TiO_2. The obtained samples had a high photocatalytic activity in hydrogen production from water–alcohol mixtures [57].

In this paper we report a novel approach for preparation of meso-nc-TiO_2 using small additives of La^{3+} ions alone and in combination with the surfactant as well as diluting of reaction mixture and their impact on the crystallinity, texture and morphology of the product.

2. Experimental

2.1. Materials

Titanium tetrabutoxide ($Ti(OBu)_4$), 1-butanol, lanthanum chloride ($LaCl_3 \cdot 7H_2O$) were obtained from Aldrich and dibenzo-18-crown-6, dodecyldimethylethyl ammonium bromide was from Fluka.

2.2. Synthesis

Meso-nc-TiO_2 was prepared using the modified sol–gel method already reported in our previous work [56]. The samples prepared under different conditions were abbreviated as TnH where n is sample number and H represents hydrothermal treatment. Molar composition of reaction mixture used for preparation of samples was:

$n=1$—1.0 TBOT: 0.12 [Na(DB18C6)]Cl: 78.0 BuOH;
$n=2$—1.0 TBOT: 0.12 [Na(DB18C6)]Cl: 0.02 DDMEABr: 78.0 BuOH;
$n=3$—0.01 La^{3+}: 1.0 TBOT: 0.12 [Na(DB18C6)]Cl: 78.0 BuOH;
$n=4$—0.01 La^{3+}: 1.0 TBOT: 0.12 [Na(DB18C6)]Cl: 0.02 DDMEABr: 78.0 BuOH;
$n=5$—0.01 La^{3+}: 1.0 TBOT: 0.12 [Na(DB18C6)]Cl: 0.02 DDMEABr: 39.0 BuOH.

Calculated amounts of reagents were consecutively dissolved in butanol. Titanium tetrabutoxide was added drop-wise with vigorous stirring. For hydrolysis, the reaction mixture was left under a glass cap (without stirring) in a humid atmosphere at room temperature until no further precipitate was formed. Half of the precipitated material has been hydrothermally treated at 175 °C for 24 h. All the samples (both treated and not treated hydrothermally) were calcined at 500 °C for 4 h to remove any remaining organic template and to improve the crystallinity of the products. The sample T05 is a gel (intermediate product in the process of synthesis of samples T5 and T5H), which was stored during 7 years at room temperature.

2.3. Characterization

X-ray diffraction patterns (XRD) were obtained on a Dron-3 M diffractometer using CuK_α ($\lambda=1.5406$ Å) radiation. The size of crystallite was estimated by applying Sherrer's equation to the FWHM of the (101) peak of anatase at $2\Theta=25.4^\circ$ with α-silicon (99.9999%) as a standard for the instrumental broadening.

The sample morphology was observed using transmission electron microscopy (TEM) on JEM 1230 "JEOL" microscope. SEM micrographs were obtained after coating the test materials with gold, using a model JSM-6060 LA "JEOL" scanning electron microscope with accelerating voltage 30 kV.

Porous structure of TiO_2 was analyzed from nitrogen adsorption/desorption isotherms measured at −196 °C using Autosorb-6 automated gas adsorption system (Quantachrome). Prior to adsorption measurements, the samples were outgassed overnight at 200 °C. Specific surface area was calculated using BET method. Pore size distributions were calculated using NLDFT method and cylindrical pore model. Total pore volume was determined as volume of nitrogen adsorbed at $p/p_0=0.997$.

3. Results and discussion

The samples of meso-nc-TiO_2 were synthesized in the experimental conditions, which were chosen on the basis of our previous studies [55–57] and careful analysis of the literature on the synthesis of mesoporous nanocrystalline TiO_2. A designated concept of the optimization of meso-nc-TiO_2 synthesis with spherical particle's morphology was formed. The concept includes a reasonable selection of the reagents (solvent, template, surfactant and lanthanum ions additives) and the conditions of the synthesis.

The type of solvent used exerts an influence on the crystallization, porosity and microstructure of TiO_2 powders obtained by hydrolysis and condensation of titanium alkoxides [33,37–40]. The effect may be caused by different influences of solvents on the condensation and aggregation of particles. For example, it is generally believed [40] that increasing the molecular weight of the alcohol leads to reducing the dielectric constant of the solvent due to lowering the electrostatic barrier to aggregation of the primary particles. Ozin and coworkers [39] chose butanol as solvent because it plays the key role in the successful synthesis of mesostructured titania. Butanol due to its relatively hydrophobic properties is able to create enhanced microphase separation between the template and the organic precursor. This allows for the formation of a well-defined mesostructure and robust inorganic framework [38].

For improving efficiency of crown ether templating activity at low concentrations the addition of small amount of surfactants was used, a technique already mentioned above [49]. It is assumed that the surfactant plays an auxiliary role by facilitating