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Morphology of Nanostructured Alumina and Lanthana Synthesized with the Use of Fibrous Organic Matrix

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Fibrous aluminum oxide γ-Al_2O_3 and lanthanum sesquioxide A-type La_2O_3 were synthesized by the thermal decomposition (700 °C, air) of cotton fibers impregnated by aqueous solutions of corresponding nitrate salts. The fibers of alumina consist of 20 nm sized particles, while the particle size of the lanthana ranges within 100–150 nm. The formation of chemisorption products on the lanthana surface is also discussed.

Keywords: Nanomaterials, Bulk-scale synthesis, Aluminum oxide, Lanthanum sesquioxide.

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1. INTRODUCTION

A growing interest in aluminum and lanthanum oxides results from their wide use in variable physicochemical applications. For example, alumina (Al_2O_3) is employed as a gas desiccant, and in the processes of fluorine extraction and oil purification. It serves as a support for metal catalysts (Ni, Pt) in organic synthesis and hydrogen-air fuel cells [1]. Alumina also plays an important role as a filling compound for different composite ceramics. Lanthanum oxide, for instance, sesquioxide (La_2O_3) is also a component of various composite materials both as a main constituent and as an additive. Lanthana additives improve optical, chemical and mechanical properties of glasses; they are used in the production of piezo- and thermoelectrical materials, in various functional ceramics [2].

The mentioned physicochemical properties of the oxides directly depend on the morphology, phase composition, and particle sizes. These parameters are in turn determined by the conditions of synthesis and following treatment. The oxides can be endowed with novel attractive properties if their particle size is reduced down to nano-scale due to the high surface to volume ratio being attained in this case.

However, nano-powders of the oxides are prone to agglomeration because of the high surface energy of the nanoparticles. Therefore it brings a particular interest to use the materials with a fibrous morphology, which simultaneously have controllable micro-dimensions and nanocrystalline structure.

2. EXPERIMENTAL

Bulk quantities of fibrous alumina and lanthana were synthesized by the thermal decomposition (700°C, air) of cotton fibers impregnated by an aqueous solution of corresponding nitrate salts $Al(NO_3)_3$ and $La(NO_3)_3$. For the clarity the obtained materials will be hereafter referred to as A-700 and L-700, respectively. For comparison, the lanthana prepared using 10-times diluted nitrate solution was also investigated. The choice of the mentioned salts is due to the lowest temperature for the synthesis of metal oxides being attained in the case of nitrates [3], and low synthesis temperature being favorable to the formation of nanosized particles.

The morphology of the fibrous oxides was studied with the use of scanning electron microscopy (Zeiss LEO SUPRA 25 electron microscope) and high-resolution transmission electron microscopy (JEM-2100 JEOL electron microscope). Elemental analyses were performed using a CHNS/O «Vario Micro cube» analyzer (for light elements) and an energy dispersive X-ray fluorescence spectrometer «X-Art M» COMITA, which is able to detect elements heavier than Mg. The specific surface area was determined using BET method. The samples were evacuated at 300°C for 2 hours before the BET measurements. It should be noted that the synthesized oxides are inevitably exposed on atmosphere, which can lead, as we will see later on, to the formation of chemisorption products on the surface of lanthana.

X-ray powder diffraction patterns were registered at room temperature, on spectrometers ARL X'TRA and DRON ADP-2-02 (CuK_α-radiation). The refinement of unit cell parameters and determination of the crystallite sizes (more exactly, the size of coherent scattering regions) was conducted by full-profile Rietveld method [4].

3. RESULTS AND DISCUSSION

The obtained fibrous oxides are tubular structures of *ca.* 500 microns in length and 2 microns in diameter, which form bundles of 10 – 20 microns in cross-section. A blow-up shows that the tubes are not uniform. Their end-faces are coarse and look like granular fractures. The specific surface area of the samples A-700 and L-700 is 280 m^2/g and 14 m^2/g, respectively.

Powder X-ray diffraction data evidence that A-700 sample contains a single crystalline phase γ-Al_2O_3 and L-

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700 sample contains a single crystalline phase of the A-La_2O_3 structural type. The latter data correspond to the literature, which reports that this is lanthanum sesquioxide that forms at the thermal decomposition of lanthanum nitrate under air [3], while at a temperature of 700°C the A-type of La_2O_3 being the most stable phase [5].

The particle size of L-700 ranges within 100–150 nm (Fig. 1). The average crystallite sizes of the A-700 and L-700 samples determined by HRTEM are 20 nm (fig. 2) and 50 nm, respectively. This agrees with the X-ray diffraction data. The use of 10-times diluted nitrate allows one to reduce the particle sizes of lanthana in 2–3 times, while the average crystallite sizes remain practically unchanged.

According to the data of X-ray fluorescence analysis the samples A-700 and L-700 contain only aluminum and lanthanum, respectively. The elemental analysis toward light elements shows the absence of nitrogen which testifies to the total decomposition of the nitrates.

In the case of L-700 one need to obtain additional information related to the presence of light elements on the surface of the sample, as it is known, that all rare earth sesquioxides (including La_2O_3) readily react with the atmosphere gases H_2O and CO_2 to form hydroxides and carbonates [6]. However formed on the surface of lanthana, these chemisorption products are known to be totally decomposed at temperatures as low as 800°C [7]. We did not perform this high-temperature heat pretreatment just before the elemental analyses. Therefore, the presence of carbon (0.67±0.09 wt%), hydrogen (0.36 ± 0.02 wt%), and oxygen (4.23±0.04 wt%) in the content of L-700 we connect with the chemisorption of atmosphere gases H_2O and CO_2 on the surface of the synthesized oxides. A layer of the chemisorption products is also seen on HRTEM images of L-700 (Fig. 3).

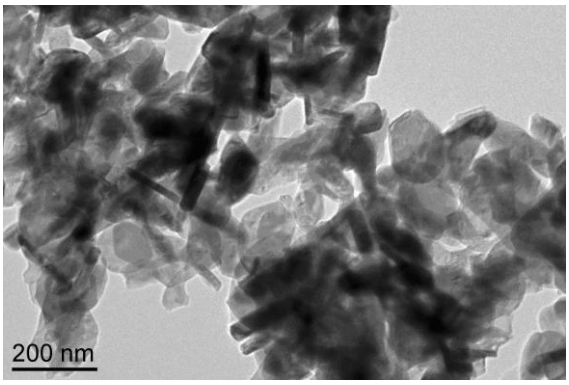

Fig. 1 – TEM image of the L-700 sample (see text)

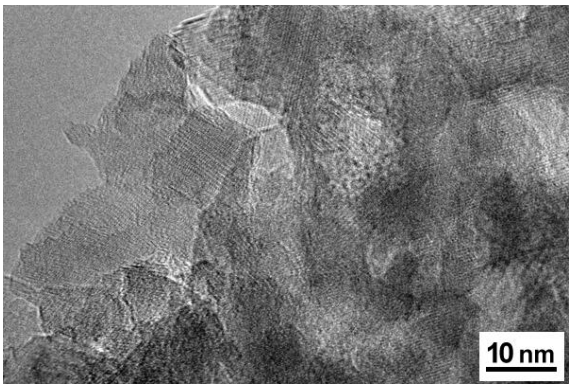

Fig. 2 – HRTEM image of the A-700 sample (see text).

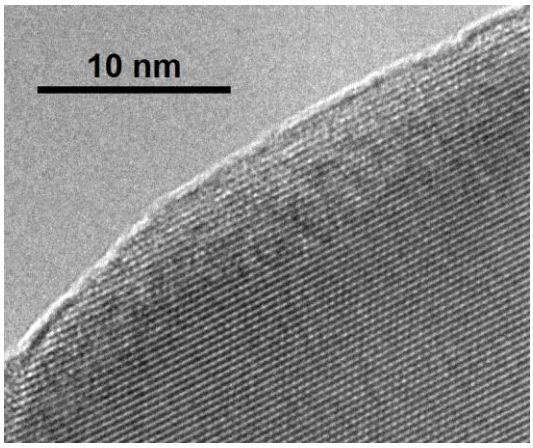

Fig. 3 – HRTEM image of the surface of L-700 (see text)

4. CONCLUSIONS

To summarize, nanostructured γ-Al_2O_3 and A-type La_2O_3 are possible to obtain in bulk by the thermal decomposition of cotton fibers impregnated by aqueous solution of corresponding nitrate salts.

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