

CERIUM(III) CARBONATE HYDROXIDE NANOPARTICLES ENCRUSTED BY METALLIC PALLADIUM. SYNTHESIS AND INVESTIGATION

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Cerium(III) nitrate and urea solution mixture were treated by hydrothermal and microwave-hydrothermal methods, as a result cerium(III) carbonate hydroxide nanoparticles (22-37 nm) were obtained. Cerium(III) carbonate hydroxide nanoparticles, encrusted by palladium were obtained using palladium reduction process from cerium(III) carbonate hydroxide solution. It is shown, that palladium occurrence disturbs hard hydrogen bond system, leading to carbonate hydroxide nanoparticles structure disorder and also increases efficiency of catalytic reactivity process.

Ключевые слова: cerium (III) carbonate hydroxide, palladium, nanoparticles, synthesis, hydrogen bonds, catalysis.

НАНОЧАСТИЦЫ ГИДРОКСОКАРБОНАТА ЦЕРИЯ, ИНКРУСТИРОВАННЫЕ ПАЛЛАДИЕМ. СИНТЕЗ И ИССЛЕДОВАНИЕ

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Из смеси растворов нитрата церия(III) и мочевины с использованием различных методов и приемов выделены наночастицы (22-37 нм) гидроксокарбоната церия(III). Путем восстановления палладия в растворах в присутствии гидроксокарбоната церия(III) получены образцы наночастиц гидроксокарбоната церия(III) с поверхностью, инкрустированной палладием. Показано, что присутствие Pd нарушает жесткую систему водородных связей матрицы и приводит к разупорядочению строения наночастиц гидроксокарбоната. Подчеркивается перспективность использования указанных композитов в катализе.

Keywords: гидроксокарбонат церия(III), палладий, наночастицы, синтез, водородные связи, катализ.

Introduction

Catalytic properties of palladium and palladium-contained nanocomposites are the topic of nowadays active investigations [1-4]. Palladium and palladium-

contained materials have been extensively used as catalysts for petroleum refinery and petrochemistry. Usage of such type catalysts in gasoline hydro-treatment technologies allows to produce high-octane isocomponents with RON 95 and with aromatic

hydrocarbons of less than 0.5 vol. %, that allows them to be used as components for the production of «Euro 5» and «Euro 4» gasoline [5–7]. Today containing platinum sulfated zirconium oxides are used as such type catalysts, but this catalyst has exploitation temperature limits (less 250°C) because of hydrogen sulfide formation. Thus, the problem of finding high-efficient catalysts has not lost its relevance.

This work is devoted to the synthesis of palladium containing composite materials based on cerium(III) carbonate hydroxide, cerium(IV) dioxide, and also to the investigation of physicochemical and structural characteristics of these materials. Combination of nanosized particles of different compounds have to improve functional characteristics of obtained materials. Also, from our point of view, existence of mixed valence states Ce^{3+}/Ce^{4+} has an effect on hydrogen mobility and as a result influences on catalytic reactivity of composite materials.

Experimental

Cerium (III) carbonate hydroxide was obtained by hydrothermal [8] and microwave-hydrothermal methods [9].

Hydrothermal method: cerium(III) nitrate ($C_{Ce} = 0.02$ mol/L) and urea (AR grade = 4 mol/L) solutions were heated to 95°C and mixed, then heated again on a water-bath for 3 minutes until the appearance of light opalescence. In the next step, solution was cooled to a room temperature in 1 hour, meanwhile white residue was observed.

The residue was centrifuged at 6000 rpm for 5 minutes and then was fivefold washed in distilled water and dried at 90°C for 6 hours.

Microwave-hydrothermal method: urea (AR grade = 0.5 mol/L) was gradually added to cerium(III) nitrate (3N purity, $C_{Ce} = 0.005$ mol/L), the obtained suspension was mixed for 2 hours on open air and then was placed into autoclave, followed by progressive heating it to 150°C in furnace (heating rate 10°C/min). Then-the-obtained cerium(III) carbonate hydroxide deposit was centrifuged at 10000 rpm for 8 minutes, fourfold washed in distilled water and dried at 30°C for 17 hours.

In order to obtain nanocomposite materials it was synthesized by the process of reducing palladium from cerium(III) carbonate hydroxide nanoparticles solution. $Ce(OH)CO_3$ was diffused in water, $PdCl_2$ (chemically pure) solution and 5 mL glycerin ($C_3H_8O_3$, chemically pure) were added to suspension, the obtained mixture was stirred for 5 minutes. In the next step the different calculated amounts of $NaBH_4$ (grade A) from 0.1 to 4 wt.% were added as a reducing agent. Deposits were centrifuged at 6000 rpm for 30 minutes, then were threefold washed in distilled water and were dried at 100°C for 5 hours. As a result, deposits of $Ce(OH)CO_3$ with different Pd contain (from 0.1 to 4 wt.%) were obtained. Then, samples were calcinated at 950°C for 24 hours and Pd encrusted samples of cerium(IV) oxide were obtained.

The particle sizes of $Ce(OH)CO_3$, CeO_2 and palladium nanocomposites were determined by the dynamic light scattering (DLS) using Beckman Coulter Delsa Nano C Particle Analyzer (Krefeld, Germany). The images of particles were obtained by using a transmission electron microscope JEOL-100CX (Japan) (accelerating voltage 80 kV, magnification 20000–50000x) and also by using TEM JEM 2100F (Japan) (accelerating voltage 200 kV). IR-spectra of samples were registered with a spectrometer (EQ-55, Bruker, Germany) in the range of wave length of 400–4000 cm^{-1} using a KBr pellet technique. The identification of final products was carried out by X-ray powder diffraction (XRD) using a diffractometer (XRD-6000, Shimadzu, Japan) with CuK α radiation at room temperature (RT). Qualitative X-ray diffraction analysis were accomplished by using computer data base ICDD PDF–2. The differential scanning calorimetry (DSC) using thermal analyzer DTAS–1300 (Russia) in air with heating rate of 8°C/min using to investigate the processes in samples during heating. Thermal decomposition analysis of carbonate hydroxides and gas phase analysis under heating were carried out with the use of thermal analysis system (STA 449 C Jupiter, NETZSCH, Germany). X-ray photoelectron spectra were registered using Riber LAS-2000 (France); C1s (285.0 eV) line responsible for bond energy was accepted as an external standard. Microwave experiments were carried out using microwave digestion system ETHOS D (Milestone, Italy), which was equipped with PTFE autoclave (power max 1000 Watt, min 10 Watt). Composite materials were analyzed using atomic absorption spectrometry (SOLAAR spectrometer with electrothermal atomization, Thermo Electron Corporation). Nitrogen content in obtained materials was investigated by automatic element analyzer EA 1112 (Thermo Finigan).

Results and Discussion

It is reported [8–10], that the hydrolysis of $Ce(NO_3)_3$ with urea is accompanied by the formation of products, containing mixture of carbonates. According to our results of chemical and X-ray analysis, carrying out of the synthesis at 85–90°C allows to obtain a single-phased cerium(III) carbonate hydroxide. It should be pointed out that nitrogen is not found in the obtained samples. Surface of synthesized compounds was analyzed by X-ray photoelectron spectroscopy; C1s (285.0 eV) line responsible for bond energy was accepted as an external standard. Results of investigation show presence of line at 884 eV in spectra samples and it corresponds to 3d 5/2 cerium(III) bond energy.

It should be stressed, that the temperature of hydrolysis influences not only on chemical composition of the reaction product but also the morphology of obtained particles. Electron microscopy and dynamic

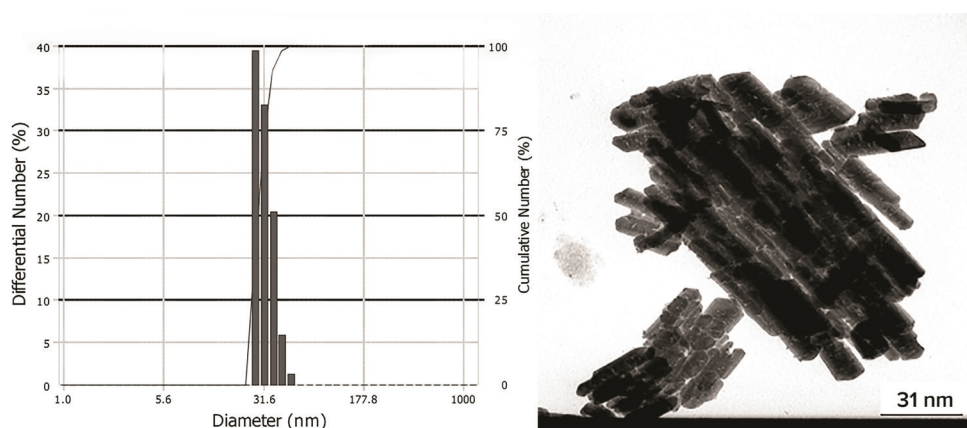


Fig. 1. Ce(OH)CO₃ particles – size distribution, obtained by DLS method (a) and nanoparticles electron micrograph (b).

It is clear that under the mixing of Ce(NO₃)₃ water solutions and urea (synthesis temperature 90±2°C), Ce(OH)CO₃ nanoparticles with oblong shape are obtained. It should be noted that right after the synthesis process these nanoparticles are in sustainable state. The obtained by two methods similar sizes of particles confirm the above statement. Increasing the time of reaction mixture heating up to 40 minutes particles grow double the size. The optimal synthesis time is 20 minutes: under lesser duration of reaction, reaction will not be completed and urea remains in mother solution, but if the period of reaction is thermostating above 20 minutes particles start to aggregate.

It was found by transmission electron microscopy (TEM), that in the case of mixing water solutions of Ce(NO₃)₃ and urea (synthesis temperature 90±2°C) the obtained nanoparticles have spherical and oblong shape (Fig.1b). Structure is porous; average the size of nanoparticles is about 60 nm and of domains is 3-4 nm.

Pd/Ce(OH)CO₃ particle-size distribution and Pd/Ce(OH)CO₃ particles electron micrograph are shown in Fig. 2. The size of obtained particles increases by at the least 25 times: from 22-37 nm (Fig. 1) up to almost 700 nm (Fig. 2a) under surface modification of Ce(OH)CO₃ by palladium.

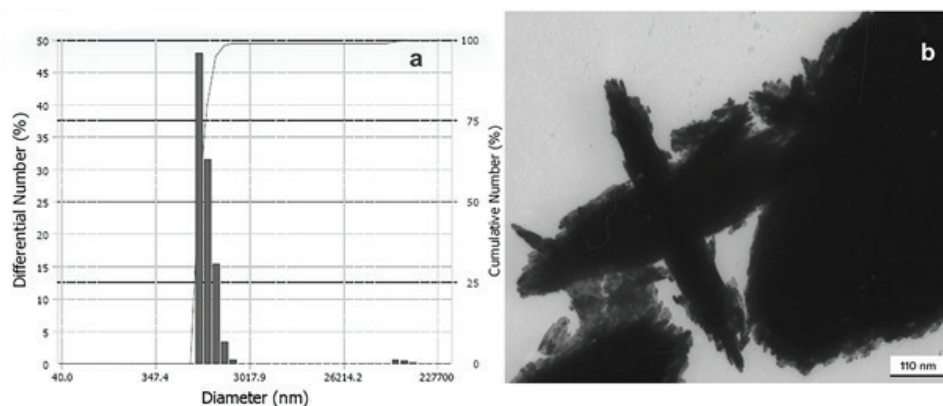


Fig. 2. Particle-size distribution of 0.82% Pd/Ce(OH)CO₃ obtained by DLS (a) and electron micrograph of the obtained nanoparticles (b).

The chemical state of palladium, applied on substrate, is an important factor, influencing on properties of the obtained materials (Fig. 3). It is found that in a 3.78% Pd/Ce(OH)CO₃ sample palladium 3d_{5/2} bond energy is 340.8 eV and is of the same value as metallic palladium; but palladium 3d_{5/2} bond energy is 336.1 eV and is of the same value as palladium oxide (PdO). The bond energy values, mentioned above, close to the values of 335.4 (Pd) and 336.8 (PdO), published in [11].

Thus, palladium exists in both states: metallic and in the form of palladium oxide (PdO). It is shown by the X-ray photoelectron spectroscopy that for

Ce(OH)CO₃ samples containing 0, 0.09 and 3.78% Pd, 3d_{5/2} lines are fixed at 884 eV bond energy, but 3d_{3/2} at 904 eV, which is of the same value as Ce(III).

The existence of strong hydrogen bond in Ce(OH)CO₃ is confirmed by the results of IR-spectroscopy investigation. Comparative study of IR spectrum was carried out for Ce(OH)CO₃ and Pd-containing Ce(OH)CO₃ composite material, heated to 230°C. According to thermal analysis, investigated materials are already free from crystallization and sorption water, but still save carbonate hydroxide shape (Fig.4).

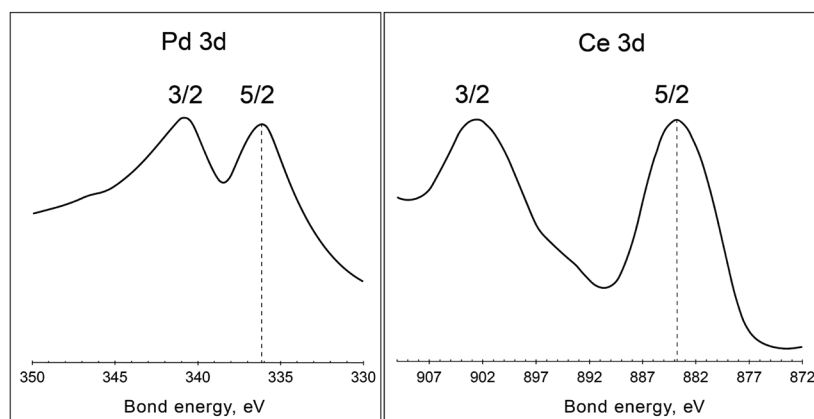


Fig. 3. X-ray photoelectron spectrum for 3.78% Pd/Ce(OH)CO₃.

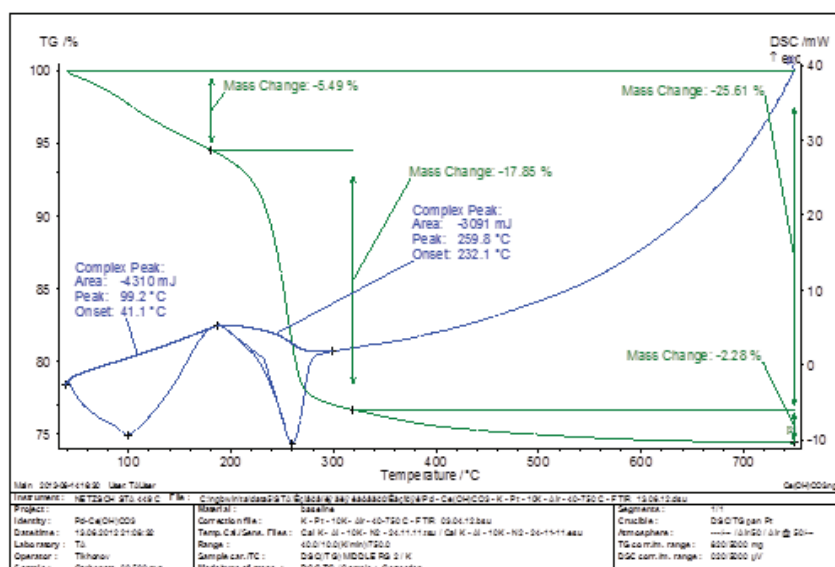


Fig. 4. DSC curves for Ce(OH)CO₃.

It is clear that IR spectrum of Ce(OH)CO₃ has an intensive absorption mode at ~3130 cm⁻¹, due to the existence of strong hydrogen bond in the structure (Fig. 5).

Absorption mode is almost absent in IR-spectrum of Pd-containing Ce(OH)CO₃ composite material. Splitting modes of twice generated valence (1550–1300 cm⁻¹) and deformation (860–700 cm⁻¹) vibrations of CO₃²⁻ group into components in Ce(OH)CO₃ spectrum which is related to reduction of anion symmetry under its coordination by metal to C_{2v} symmetry group [12]. Thus, there is only one mode (1076 cm⁻¹) for CO₃²⁻ ion breathing valence vibration, but in the range of doubly generate valence vibrations of Ce(OH)CO₃ there are 16 components (including weakly defined shoulders and bends of spectrum). This is suggesting that there are at least 8 sets of CO₃²⁻ groups put in order. Mentioned complexity of this spectrum area, taking into account that there is only one mode of breathing valence vibration, can be connected with formation of domain structure of nanoparticles and different anion orientation in domains.

Quantity of twice generated valence vibrations severely decreases in the IR-spectrum of 1% Pd-containing Ce(OH)CO₃ material, which can be evidenced about anion distribution positions in crystal lattice. This fact is confirmed by comparing of high resolution photomicrographs of investigated materials (Fig. 6).

On the base of obtained experimental data analysis, it is suggested, that Ce(OH)CO₃ nanoparticles are built from blocks with ordered structure, which sizes are no more than 10-15 nm (Fig. 6a), while nanoparticles Ce(OH)CO₃, containing Pd, are demonstrated in complete disorder. It is not improbable that the presence of Pd nanoparticles on Ce(OH)CO₃ surface induces higher mobility of protons in OH-groups. High velocity of protons exchanging leads to the destruction of strong hydrogen bonds and to averaging of effects, observed in presented above results of microscopical analysis. However, such appearance of the microphotographs of nanoparticles with Pd, is due to the presence of thin metal coating on the particle's surface.

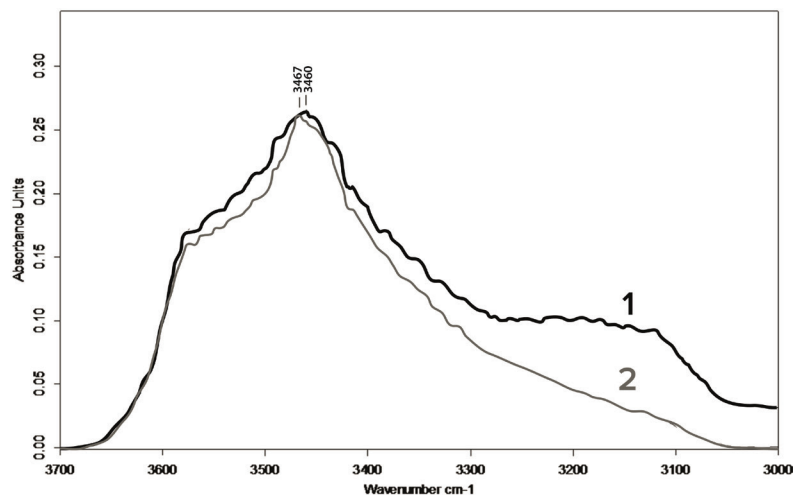


Fig. 5. IR spectra in the frequency range 3700–3000 cm^{-1} for $\text{Ce}(\text{OH})\text{CO}_3$ (1) and 1% Pd-containing $\text{Ce}(\text{OH})\text{CO}_3$ composite material (2). IR spectra were registered after heating at 230°C.

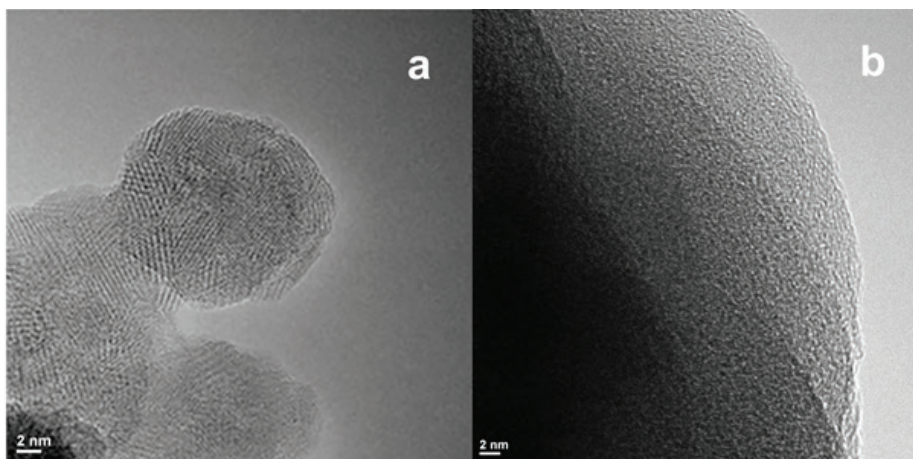


Fig. 6. High resolution photomicrographs of $\text{Ce}(\text{OH})\text{CO}_3$ (a) and 0.85% Pd/ $\text{Ce}(\text{OH})\text{CO}_3$ (b).

The size measurement of particles, obtained by $\text{Ce}(\text{OH})\text{CO}_3$ calcination, is carried out by two methods: the dynamic light scattering and transmission electron microscopy. It is clear, that particles, formed as a result of

$\text{Ce}(\text{OH})\text{CO}_3$ calcination, have a form close to spherical. The average size of these particles is 16-33 nm, though during long calcination particles agglomerate into aggregates sized between 1000–1200 nm (Fig. 7).

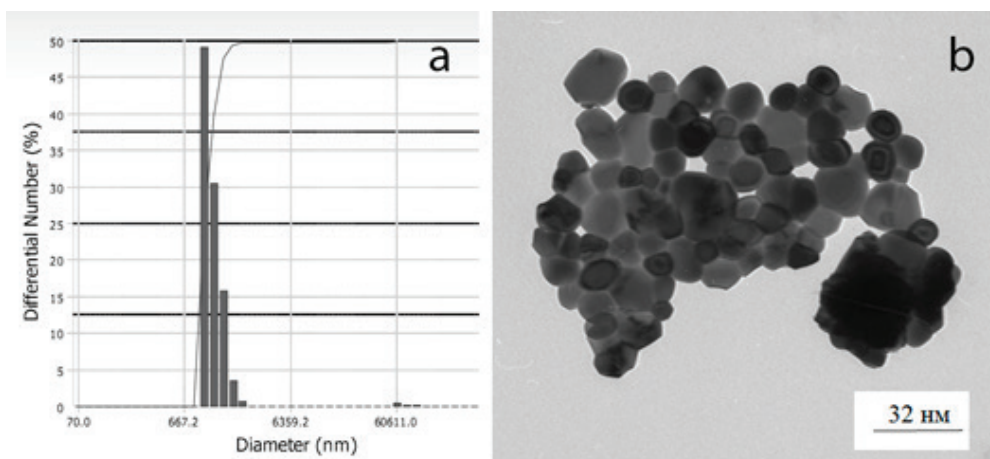


Fig. 7. Particle-size distribution of 1.52% Pd/ CeO_2 obtained by DLS (a) and electron micrograph of the obtained nanoparticles (b).

As a result of carried-out work is shown the synthesis ability of $\text{Ce}(\text{OH})\text{CO}_3$ nanoparticles (22–37 nm) in conditions of hydrothermal and hydrothermal-microwave processing in cerium nitrate(III) and urea mixture solutions. Cerium(III) carbonate hydroxide nanoparticles, encrusted by palladium were obtained using palladium reduction process from cerium(III) carbonate hydroxide solution. Complex investigations showed, that palladium exists on the nanoparticles surface in both states: metallic and in the form of palladium oxide (PdO). It also showed, that the Pd presence, due to an active and fast proton exchange, destroys strong hydrogen bond system of $\text{Ce}(\text{OH})\text{CO}_3$, that leads to a distortion of its structure and in turn, highly probably, to an increase of the efficiency of the catalytic process.

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