

SINTEZA NANOPARTICULELOR DE OXID DE CERIU CU MORFOLOGIE CONTROLATĂ

SYNTHESIS OF CERIA NANOPARTICLES WITH CONTROLLED MORPHOLOGY

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Ceria nanoparticles were synthesized by two different wet soft chemistry routes, the thermal decomposition of a tartrate-based precursor and the reverse microemulsion method. The tartrate-based precursor was characterized by FTIR spectroscopy and thermal analysis, whereas the sample isolated from the microemulsion by X-ray diffraction. The precursors were calcined at 500°C, 3h in air and oxide nanopowders were investigated by X-ray diffraction, transmission electron microscopy and selected area electron diffraction. Ceria sample obtained by decomposition of tartrate-based precursor has nanoparticles in the range of 6 - 12 nm with a slight tendency of agglomeration and a specific surface area of 28 m²/g, whereas the sample synthesized by reverse microemulsion method has nanoparticles of 6 nm average size, with very narrow size distribution, and higher specific surface area, 68 m²/g.

Nanoparticulele de oxid de ceriu s-au obținut prin două tehnici neconvenționale de sinteză, descompunerea termică a unui precursor pe bază de tartrat și metoda microemulsiilor inverse. Precursorul de tip tartrat s-a caracterizat prin spectroscopie FTIR și analiză termică, iar proba rezultată după îndepărtarea microemulsiei, prin difracție de raze X. Precursorii au fost calcinați la 500°C, 3h, în aer și nanopulberile oxidice au fost investigate prin difracție de raze X, microscopie electronică în transmisie și difracție de electroni pe arie selectată. Proba de oxid de ceriu obținută prin descompunerea precursorului de tip tartrat se prezintă sub formă de nanoparticule cu dimensiuni între 6 și 12 nm, cu o ușoară tendință de aglomerare, având o suprafață specifică de 28 m²/g, în timp ce proba sintetizată prin metoda microemulsiilor inverse este constituită din nanoparticule cu dimensiunea medie de 6 nm, cu o distribuție îngustă a dimensiunilor și o suprafață specifică mai mare, 68 m²/g.

Keywords: ceria nanoparticles, reverse microemulsion, thermal decomposition method, tartrate-based precursor

1. Introduction

Ceria is one of the most studied oxides in the last twenty years. It was extensively investigated as catalyst [1,2] or catalyst support [3], UV absorber [4], gas sensor [5], optic material [6], abrasive powder [7] and solid oxide electrolyte in SOFC [8]. Recently, it was discovered that CeO₂ nanoparticles have scavenger properties against radical oxygen species (ROS) that could be useful in the prevention of retinal [9] and neuronal degeneration [10]. The nanoparticle size is one of the key factors in all these applications, especially in the biomedical ones. In order to control the particle size distribution, several methods have been developed. Cubic CeO₂ crystals of 2-3 nm were obtained by surfactant assisted method in subcritical conditions. By auto-assembling processes of ceria nanocubes, driven by the variation of time and calcination temperature, 1D (nanorods) and 2D (nanoribbons) could be prepared [11]. The synthesis under hydrothermal conditions, 277 °C, 24h, using cerium oxalate and different aminoacids, led to a fiber-like morphology of nanocrystalline and mesoporous ceria [12]. Using polymer (PS or PMMA) nanospheres as hard template deposited on a filter surface and impregnated with a cerium chloride

aqueous solution and then treated with ammonia solution, a reverse opal ceria mesostructure was obtained after the calcination at 300°C [13]. A better control of the particles size was achieved when the reverse microemulsion method was employed, using a nonionic surfactant (Marlophen NP5), an organic solvent (*n*-heptane) and cerium nitrate aqueous solution [14]. After precipitation with ammonia solution, separation and calcination, cubic ceria particles with the size between 2 and 6 nm were obtained by varying the water / surfactant ratio, R_w , in the range of 5.8 – 16.4 [15]. A simple and environmental friendly method is the precipitation at room temperature or precipitation-decomposition method. Studies on the various synthesis parameters as aging time, temperature, pH and calcination temperature proved their influence on the morphology and catalytic properties of ceria nanoparticles [16].

Our paper presents a comparison between two synthesis methods of CeO₂ nanoparticles and significant improvements for both methods are disclosed here, the use of gaseous ammonia as precipitation agent in the reverse microemulsion and tartaric acid as chelating compound in the thermal decomposition method.

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2. Experimental

2.1. Synthesis of cerium oxide nanoparticles

CeO₂ samples were obtained by two different wet chemical techniques, the thermal decomposition of a tartrate-based precursor and the reverse microemulsion synthesis, respectively. All the chemicals are analytical grade and were purchased from Sigma-Aldrich.

Thermal decomposition of tartrate-based precursor. To the 0.5 M aqueous solution of Ce(NO₃)₃, solid tartaric acid was added in a molar ratio, cerium nitrate : tartaric acid, 1:2. Then, by dropping 0.5 M ammonia aqueous solution, the pH was kept at 4 and the reaction mixture was refluxed for 7 hours, cooled and precipitated in ethanol with a white tartrate-based precursor formation. The complex precursor was filtered off, washed several times with ethanol and dried at 100 °C. Cerium oxide nanoparticles were obtained by calcining the complex precursor at 500 °C, 3h with a heating rate of 10 °/min.

Synthesis of ceria nanoparticles by reverse microemulsion method. Ceria nanoparticles were synthesized in the “nanoreactors” of reverse micelles formed from cetyltrimethylammonium bromide (CTAB) as cationic surfactant, *n*-butanol as cosurfactant, and an aqueous solution of (NH₄)₂Ce(NO₃)₆ in isooctane. The transparent microemulsion was prepared by adding 9 mL 0.2 M solution of (NH₄)₂Ce(NO₃)₆ to the organic phase obtained by dissolving 15 g CTAB in 180 mL isooctane and 105 mL *n*-butanol. The precipitating agent, gaseous ammonia produced by boiling a 28% aqueous ammonia solution and dried on silicagel, was bubbled into the microemulsion at room temperature, under magnetic stirring, for 6 h, until a yellow precipitate was formed and separated by centrifugation, washed with ethanol several times to remove the surfactant, and dried at 70 °C overnight. Ceria nanoparticles were obtained by annealing the precursor powder at 500 °C, 3h, with a heating rate of 3°C/min.

In both methods, the calcining parameters were carefully selected in order to eliminate completely the organic compounds and to avoid the particles agglomeration.

2.2. Sample characterization

The tartrate-based precursor was analyzed by thermal analysis (DTA-TG) and infrared spectroscopy. The thermal analysis was performed on a Shimadzu DTA-TA-51H equipment, in 20° - 1000 °C temperature range, in air. The FTIR spectra were collected with a Bruker Tensor 27 spectrophotometer. A Rigaku Miniflex 2 diffractometer was used to identify the crystalline phases of the ceria nanoparticles. The morphology of the obtained nanoparticles was investigated by high-resolution transmission electron microscopy (HRTEM) using a Philips Tecnai F30 G² S-Twin

transmission electron microscope operated at 300 keV. Specific surface area measurements were performed on an Autosorb iQ2 MP equipment.

3. Results and discussion

In the FT-IR spectrum of the TA-based precursor (Fig. 1), it can be noticed, beside the characteristic vibration modes of NO₃⁻ anions at 1385 cm⁻¹, the stretching vibrations of carboxyl group shifted to lower frequencies ($\nu_{\text{asCO}} = 1599\text{cm}^{-1}$ and $\nu_{\text{asCO}} = 1390\text{cm}^{-1}$) than those characteristic for tartaric acid, and OH characteristic vibrations modes (from 3410 cm⁻¹ and 3320 cm⁻¹) also shifted to lower frequencies at 3380 and 3233 cm⁻¹, respectively, which prove that the tartrate anion acts as chelating agent.

The TG-DTA analysis of tartrate-based precursor showed the decomposition of the complex compound ended with a large exothermic effect at 305°C (Fig. 2) assigned to the burning of the organic groups. Therefore, in agreement with TG-DTA results, to obtain the crystalline ceria nanoparticles, the precursor was calcined at 500 °C, 3h.

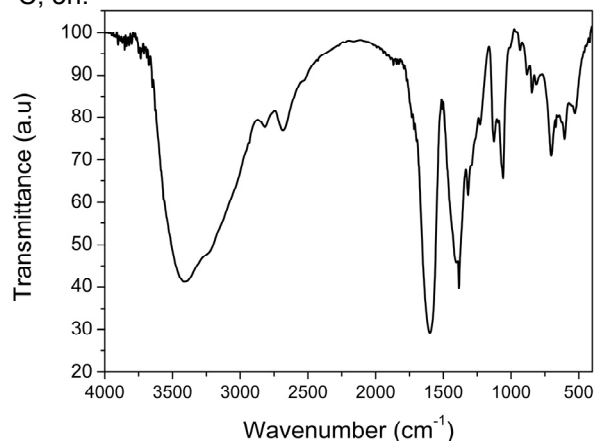


Fig. 1 - FTIR spectrum of tartrate-based precursor / *Spectrul FTIR al precursorului pe bază de tartrat.*

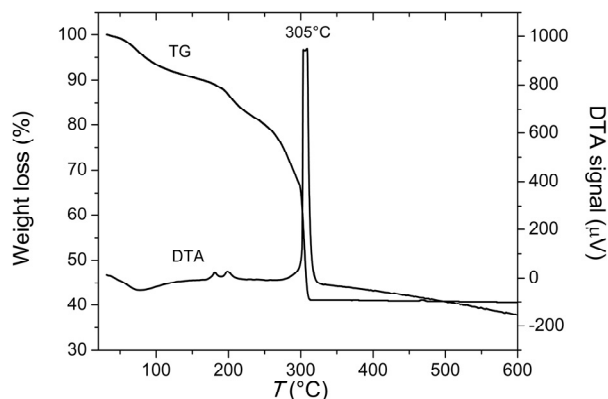


Fig. 2 - TG-DTA analyses of tartrate-based precursor / *Analiza TG-DTA a precursorului pe bază de tartrat.*

Structural characterization of CeO₂ samples obtained at 500 °C was performed by X-ray

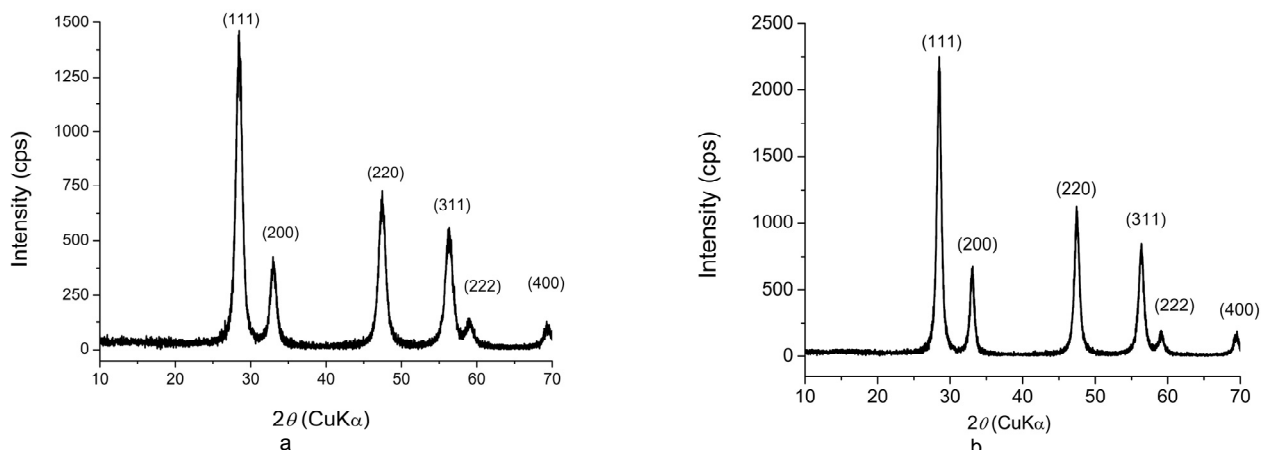


Fig. 3. - XRD patterns of CeO_2 samples calcinated at 500°C , obtained by reverse microemulsion method (a) and thermal decomposition method (b). / Difractogramele de raze X ale probelor de CeO_2 calcinate la 500°C , obținute prin metoda microemulsiilor inverse (a) și metoda descompunerii termice (b).

diffraction (XRD). For both methods, the XRD data of CeO_2 samples indicated the formation of the fluorite type structure, with cubic symmetry (ICDD 81-0792) characteristic for ceria (Fig. 3). The crystallite size of CeO_2 nanopowders calculated from XRD data using PDXL software were 6 nm for the inverse microemulsion method and 11 nm for the thermal decomposition technique, respectively. XRD data confirm the fluorite structure formation with cubic symmetry even for the samples obtained at room temperature and separated from microemulsion (Fig. 4). It can be noticed that the annealing treatment determined an increase of the crystallite size from 4 nm to 6 nm. The BET specific surface area values of the samples were $68 \text{ m}^2/\text{g}$ and $28 \text{ m}^2/\text{g}$ for the microemulsion method and thermal decomposition method, respectively, in agreement with literature data [17,18].

The morphology of cerium oxide samples was investigated by transmission electron microscopy. From the TEM investigation of ceria nanoparticles obtained by the decomposition of tartrate-based precursor, it was noticed that the nanoparticles had a slightly tendency to form nanometric spherical agglomerates (Fig. 5a). The size of the primary particles was in the range of 6-12 nm, as HRTEM images (Fig. 5b) proved. Ceria

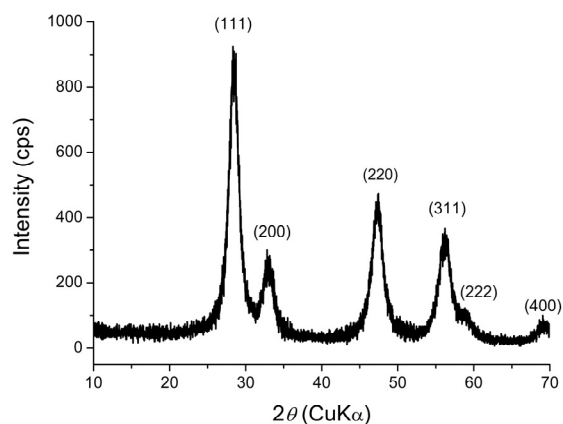


Fig. 4. - XRD patterns of the sample isolated from the microemulsion / Difractograma de raze X a probei izolate din microemulsie.

obtained by the reverse microemulsion method had a narrow particle size distribution with the average size of 6 nm calculated from TEM (Fig. 6a) and HRTEM (Fig. 6b) images. Selected area electron diffraction, SAED, analysis (Figures 5 and 6 insets) showed that both samples were crystalline ceria with fluorite structure and cubic symmetry.

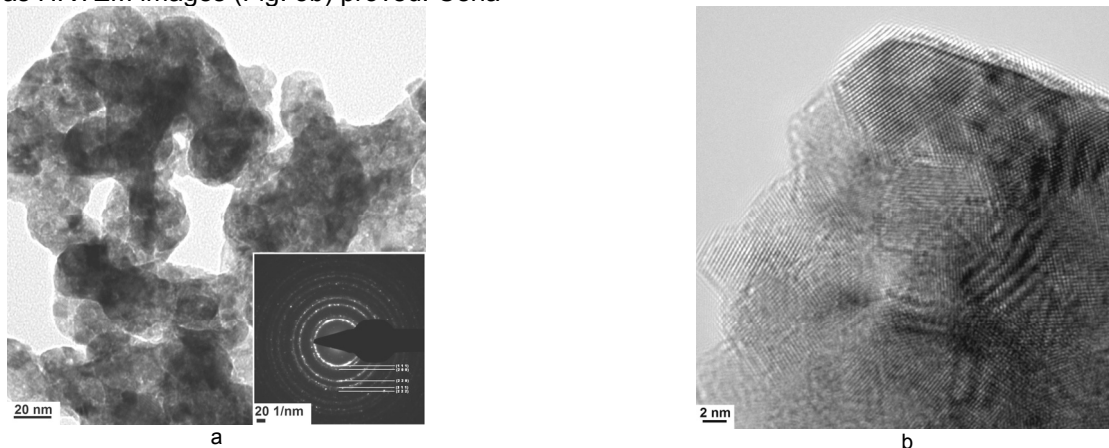


Fig. 5 - TEM and HRTEM images of CeO_2 sample obtained by thermal decomposition method (inset, SAED analysis) / Imaginile TEM și HRTEM ale probei de CeO_2 obținute prin metoda descompunerii termice (insetată, analiza SAED).

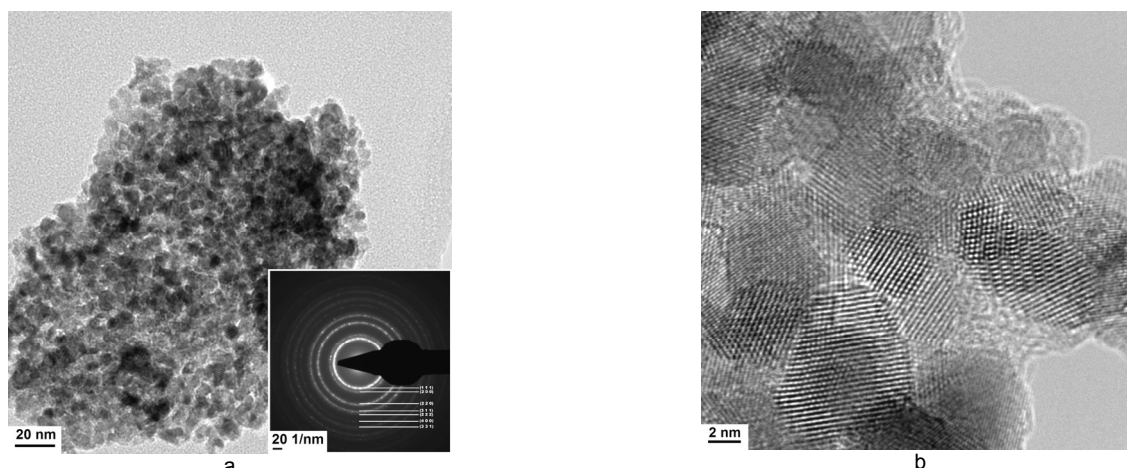


Fig. 6 - TEM and HRTEM images of CeO₂ sample obtained by reverse microemulsion method. (inset SAED analysis) / Imaginile TEM și HRTEM ale probei de CeO₂ obținute prin metoda microemulsiilor inverse (inserată, analiza SAED).

The results showed that CeO₂ nanoparticles were obtained by both methods, but with different morphology. In the case of the thermal decomposition of tartrate-based precursor, the elimination of the remaining organic parts, even at low temperature, 500°C, induced a certain degree of agglomeration that could not be avoided. This fact is characteristic for the obtaining of oxide nanoparticles by thermal decomposition of complex precursors.

It is well known that the reverse microemulsion method allows the synthesis of monodisperse ceria nanoparticles and the control of their morphology by setting the water/oil molar ratio, $R_{W/O}$, at constant value [16]. The variation of $R_{W/O}$ parameter during the adding of the precipitation agent as a secondary emulsion or directly, as an aqueous solution is a major drawback of this method. The parameter $R_{W/O}$ varies from the initial moment of adding the precipitation agent, until the new emulsion is formed and stabilized, and the value could significant increase when the precipitation agent is added as aqueous solution. These variations of $R_{W/O}$ values accompany the precipitation process and finally affect the particle size, broadening the monomodal particle size distribution. By the modification of the method proposed in this work, precipitation of ceria particles does not occur as a result of intermicellar interactions, but as a mass transfer from gaseous phase to micelles, preserving the initial characteristics of the microemulsion, including the stability and the value of $R_{W/O}$. This new approach of the microemulsion method, when it is possible, allows a better control of the particles morphology.

4. Conclusions

Ceria nanoparticles were obtained by two soft chemistry routes. Better results in terms of nanoparticle dimension, their size distribution and specific surface area were obtained in the case of

reverse microemulsion method than for the thermal decomposition technique. These differences could be explained by the burning of the organic part of the tartaric precursor in the calcination step that contributed to the nanoparticles agglomeration. By the other hand, the nanoreactors generated by the reverse microemulsion conditions, constrained the synthesized ceria nanoparticles to a limited size. Also, a key factor in obtaining of monodisperse nanoparticles with a narrow size distribution was the bubbling of ammonia gas directly into the emulsion, instead of mixing with a second emulsion containing ammonia solution, which allowed the preservation of the initial concentration of cerium ions in each nanoreactor during the chemical reaction.

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RECENZIE / REVIEW

Nicolae Şt. Noica

**Palatul Academiei de Înalte Studii Comerciale și Industriale
și personalități din lumea construcțiilor**

Palatul Academiei de Înalte Studii Comerciale și Industriale și personalități din lumea constructorilor



Autor : NICOLAE Şt. NOICA

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110 pagini, 27 portrete, 70 ilustrații color, 70 facsimiluri

În anul 2013 s-a sărbătorit centenarul Academiei de Înalte Studii Comerciale și Industriale înființată ca urmare a propunerii ministrului Industriei și Comerțului, Nicolae Xenopol (fratele istoricului Alexandru Xenopol și al arhitectului Filip Xenopol), prin Înalțul Decret Regal nr.2978 din 6 aprilie 1913, semnat de regele Carol I.

La 1 noiembrie 1913 școala și-a deschis cursurile cu aproape 700 studenți și studente într-o clădire de pe Calea Victoriei, lângă Fundația Universitară "Carol I", actuala Bibliotecă Centrală Universitară (clădire care ulterior a fost demolată).

Pentru construcția localului Academiei, rectorul Stanislas Cihoski încheie la 11 iunie 1923 un contract cu profesorul inginer-arhitect Grigore P. Cerchez pe care „îl însărcinează să facă planurile de arhitectură și să conducă lucrările respective”. Acesta alege printre colaboratori pe arhitectul Edmond Van Saanen Algi (mama fiind româncă iar tatăl olandez), care mai târziu preia conducerea lucrărilor.

Apoi construcția actualului "Palat din Piața Romană" a fost încredințată antreprizei arhitectului Grigore G. Cerchez cu care s-a încheiat contractul la 2 mai 1924 pentru suma de 19.895.540 lei. Lucrările au început la 4 mai 1924, la 3 iulie 1926 s-a organizat licitația pentru lucrările de zugrăveli și vopsitorie, construcția palatului fiind finalizată în octombrie 1926 iar la 15 noiembrie 1926 a avut loc inaugurarea. "Cu acest prilej, a fost întocmit un act comemorativ și s-a făcut sfințirea localului în prezența A.S.R. Prințesa Mamă Elena, a patriarhului Miron Cristea, ministrului Industriei și Comerțului Mihai Berlescu, ministrului Instrucțiunii Publice Petre P. Negulescu, ministrului Muncii și Asigurărilor Sociale Grigore Trancu Iași, rectorului dr.I.N.Angelescu."

"Merită să amintim grija deosebită pe care înaintașii noștri o aveau pentru cheltuirea banului public, așa cum reiese din documentele încheiate și păstrate cu respect la Arhivele Naționale (tabloul cu toate plățile făcute pe ani și luni pentru construcția palatului)".

În prefața cărții, domnul academician Mugur Isărescu scrie: "Aici, la ASE am urmat cursurile universitare, am devenit economist, cercetător în domeniul conjuncturilor mondiale și dascăl; aici predau și în prezent teoria și practica monetară. E școala mea. Am fost din totdeauna mândru de școala mea – unde an de an învață mii de studenți și predau mari profesori – e găzduită într-un palat impunător în centrul Bucureștilor; o clădire monumentală, de patrimoniu, care își are un loc binemeritat în constelația palatelor bucureștene care au făcut faima "Micului Paris". Și care sunt și azi, monumente care se numără printre marile atracții ale capitalei României".

În continuare se referă la cele cinci volume dedicate Palatelor din București pe care autorul Nicolae Noica le-a scris și pe care îl numește "istoric al zidurilor". Și Palatul din Piața Romană face parte integrantă din constelația acestor clădiri reprezentative, adevărate monumente de arhitectură, construite de cei mai valoroși constructori și arhitecți români, pe care autorul îi evocă cu mult respect și prețuire. Autorul pune accentul pe profesionalismul acestor personalități, pe devotamentul și vocația lor pentru lucrul bine făcut. Și se întreabă: "dacă înaintașii noștri au putut, noi de ce n-am putea" ?

VIRGINIA MOLDOVEANU
