

CHEMISTRY

Synthesis of Spherical Oxide Particles in Microwave Hydrolysis of Zr(IV), Ce(IV), and Ni(II) Salt Solutions

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Elaboration of the methods used to synthesize spherical oxide particles is important in designing new ceramic and catalytic materials [1]. Among the numerous methods suggested for preparing spherical particles, the sol–gel method is currently the most promising. In particular, Ogihara *et al.* [2] synthesized a monodisperse ZrO_2 powder through alkaline hydrolysis of zirconium butoxide. The morphology of the resulting particles and their size distribution strongly depend on the concentration of the initial alkoxide and water/alkoxide ratio. Li and Messing [3] obtained spherical ZrO_2 particles by adding excess isopropyl alcohol to a partially hydrolyzed concentrated solution of zirconyl salts; however, the resulting oxide powder had a wide size distribution.

Note that, typically, methods of “mild chemistry” do not permit the use of highly concentrated solutions, which considerably worsens their efficiency. Thus, it is important to elaborate a new method that would allow one to rapidly obtain spherical oxide particles with a narrow size distribution from rather concentrated solutions.

This problem could be solved by exposing salt solutions to microwave radiation in the course of hydrolysis [4, 5]. In particular, Komarneni *et al.* [6–8] showed that the rate of the hydrothermal synthesis of different oxide powders can be increased under microwave radiation by several orders of magnitude.

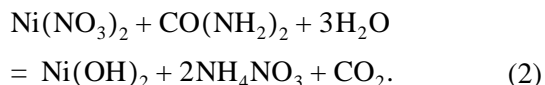
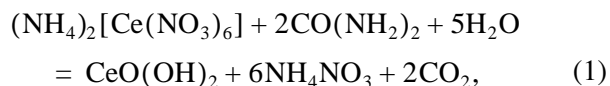
In this paper, we report on new methods for the synthesis of oxide powders through microwave-assisted hydrolysis of concentrated aqueous and aqueous–alcohol salt solutions, which make it possible to obtain spherical oxide particles with a narrow size distribution. Special attention was focused on studying the effect of the microwave treatment parameters and the nature of the solvent on the formation, morphology, and character of size distribution of oxide particles.

EXPERIMENTAL

The following reagents were used: $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (all of analytical grade), and $(\text{NH}_2)_2\text{CO}$ (reagent grade). Solutions were heated in a Samsung M1712R microwave oven (maximum output power, 850 W; microwave frequency, 2.45 GHz).

Hydrolysis of Zr(IV) salts in aqueous–alcohol solutions. Initial aqueous–alcohol solutions were prepared from distilled water and ethyl, propyl, isopropyl, or *tert*-butyl alcohols or glycerol. These solutions were mixed with aqueous solutions of zirconyl salts, $\text{ZrO}(\text{NO}_3)_2$ or ZrOCl_2 in ratios such that the zirconium concentration was 0.128 M and the alcohol-to-water ratio was 5 : 1. The initial solution in a glass flask was placed in a microwave oven (input power, 300 W). The solution was heated to the boiling point (3–5 min), and the oven was switched off. Then, the solution was neutralized with a 20% ammonia solution, which prevented the precipitate formed in the course of microwave hydrolysis from being dissolved on cooling. This precipitate was centrifuged (4000 rpm, 10 min), washed with distilled water until the reaction toward Cl^- and NO_3^- was negative, dried at 60°C for 3 h, and annealed at 400°C for 6 h.

Hydrolysis of Ni(II) and Ce(IV) salts in aqueous solutions in the presence of urea. To 0.4 M aqueous solutions of the Ni(II) or Ce(IV) salt, stoichiometric amounts of urea were added in accordance to the schemes



The resulting solutions in a glass flask were placed in a microwave oven (input power, 100 W) and boiled for 1 h. The nascent precipitates were centrifuged (4000 rpm, 10 min), washed with distilled water until the reaction toward NO_3^- was negative, dried at 60°C for 3 h, and annealed at 200°C for 24 h.

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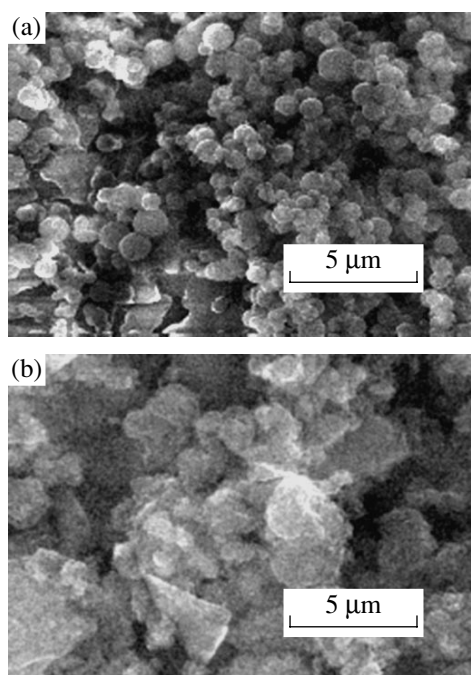


Fig. 1. SEM microphotographs of ZrO_2 powders obtained by hydrolysis of a ZrOCl_2 solution in a isopropyl alcohol–water mixture. Here and in Fig. 2, (a) microwave treatment and (b) conventional heating.

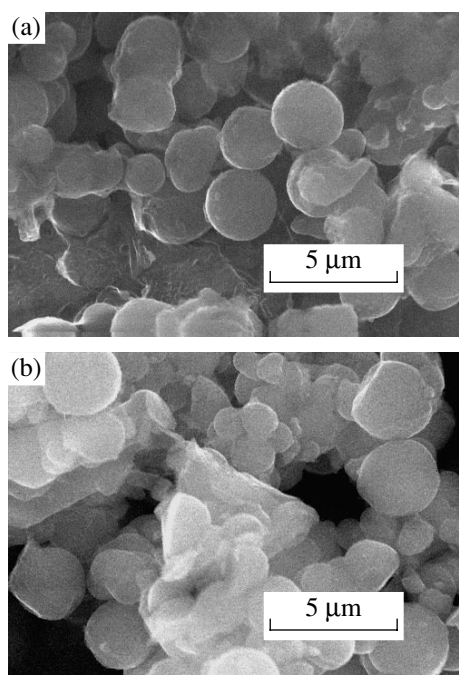


Fig. 2. SEM microphotographs of CeO_2 powders obtained by hydrolysis of a $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ solution.

Analysis. The phase composition and the degree of crystallinity of the resulting oxide samples were monitored by X-ray powder diffraction. X-ray powder diffraction patterns were recorded on a DRON-3M ($\text{CuK}_{\alpha 1}$ radiation) and analyzed with the use of the JCPDS database. The average size of coherent-scattering domains (CSD) D was determined by harmonic profile analysis of diffraction maxima. Patterns were recorded pointwise with an increment of 0.01° and a counting time of 10 s. To consider the instrumental line broadening, α -quartz was used.

The average CSD size was estimated using the Seelyakov–Scherrer formula

$$D = \frac{\lambda}{\beta \cos \theta},$$

where λ is the X-ray radiation wavelength (nm) and β is the physical broadening (rad). The error in determination of D was 8–10%.

Morphology and size distribution parameters were studied by scanning electron microscopy (SEM) on a Jeol JEM-2000FX microscope (accelerating voltage 200 kV). To provide discharge, powders were stuck on a copper plate using a conducting (silver) glue.

Specific surface area was measured by the BET method using a Micromeritics ASAP 2100 surface area analyzer employing nitrogen as the adsorbate. The analyzer was calibrated using an Al_2O_3 powder with a known specific surface area.

RESULTS AND DISCUSSION

As is known, adding an alcohol to an aqueous salt solution decreases its dielectric constant, which leads to a decrease in solvation energy, oversaturation of the solution, and deposition of a precipitate. This effect is used for salting-out [9]. Similar changes are observed on heating aqueous–alcohol salt solutions, because the dielectric constant decreases with an increase in temperature.

Our experiments showed that when glycerol is used as a component of a water–alcohol mixture, deposition is absent. Upon microwave-assisted heating of the ethyl alcohol–zirconyl salt–water system, the reaction is not completed, which is indicated by the small amount of precipitate formed and by the presence of ZrO^{2+} ions in the solution. At the same time, using propyl, isopropyl, and *tert*-butyl alcohols results in exhaustive hydrolysis, which is supported by the absence of ZrO^{2+} ions in the mother liquor after the precipitate is separated. Microwave treatment of the *tert*-butyl alcohol–zirconium salt–water system leads to deposition of the initial salt ($\text{ZrO}(\text{NO}_3)_2$, ZrOCl_2), which is supported by TGA data. Thermal analysis of the powders deposited from solutions with ethyl and isopropyl alcohols showed that the overall weight loss was 25–26% in both cases. This is consistent with the theoretical weight loss of 22.61% for $\text{Zr}(\text{OH})_4$ or $\text{ZrO}(\text{OH})_2 \cdot \text{H}_2\text{O}$.

X-ray powder diffraction showed that the as-deposited samples were amorphous and annealing these samples at 400°C for 6 h led to the formation of pure tetra-

Table 1. Specific surface areas of oxide powders as probed by the BET method

Oxide	Microwave hydrolysis, m ² /g	Conventional hydrolysis, m ² /g
NiO	130.9	64.7
CeO ₂	76.1	106.6
ZrO ₂	19.7	40.3

Table 2. CSD size in the resulting oxide powders

Oxide	Microwave hydrolysis, nm	Conventional hydrolysis, nm
NiO	5.0	8.9
CeO ₂	7.3	6.0
ZrO ₂	18.0	16.8

gonal ZrO₂. As can be seen in the SEM microphotographs (Fig. 1) of ZrO₂ samples deposited from solutions containing propyl or isopropyl alcohol, microwave treatment leads to the formation of tiny particles (0.5–1.5 μm) of nearly ideal spherical shape, whereas hydrolysis upon conventional heating results in the formation of large conglomerates of irregular shape.

Using urea makes it possible to maintain a low constant concentration of the precipitating agent, which results in the formation of fine, nonconglomerated particles of desired morphology. Thermal and microwave treatment of solutions of nickel and cerium salts in the presence of urea led to the formation of amorphous precipitates. X-ray powder diffraction showed that annealing the as-prepared deposits at 250°C for 24 h resulted in single-phase nickel oxide or cerium dioxide. As follows from the SEM microphotographs (Fig. 2), hydrolysis upon both microwave and conventional heat treatment leads to cerium dioxide particles of predominantly spherical shape. Note that nonuniformly supplying heat to heat-treated solutions results in the formation of a considerably larger amount of irregular particles, whereas almost all particles obtained upon microwave treatment have a nearly spherical shape.

Both the microwave and conventional hydrolysis of nickel nitrate in the presence of urea lead to the formation of irregular particles. This seems to be due to a relatively high solubility of nickel hydroxide; this renders the hydrolysis process reversible to a considerably larger extent, which prevents the formation of particles of regular shape. At the same time, particles obtained through microwave hydrolysis are characterized by a

considerably higher dispersity and a narrower size distribution.

As follows from the BET analysis of the samples, the surface area of oxide powders depends strongly on the mode of heat supply upon hydrolysis (Table 1). Microwave treatment can both increase (NiO) and decrease (CeO₂, ZrO₂) the specific surface area in the oxides under study. These results are in good agreement with the estimations of the average CSD size *D* (Table 2). We may assume that the different character of changes in the dispersity of samples subjected to microwave treatment is caused by the different microwave absorbing powers of the corresponding metal hydroxides, which is related to their dielectric properties.

Therefore, we found that microwave treatment of aqueous and aqueous–alcohol solutions of Zr(IV), Ce(IV), and Ni(II) salts results in their exhaustive hydrolysis, producing the corresponding hydroxide products. Microwave hydrolysis makes it possible to obtain particles of predominantly spherical shape and with a narrower size distribution as compared to hydrolysis under conventional heating. Microwave treatment can both decrease and increase the specific surface area and average dimensions of crystallites of the nascent oxide phases.

ACKNOWLEDGMENTS

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