Microwave-assisted synthesis of cerium oxide nanoparticles

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Cerium oxide has recently received a lot of attention as a consequence of its catalytic properties that make it attractive for a wide range of applications ranging from solid oxide fuel cell, to three way catalysts gas sensors, etc. Although several methods have been proposed for the synthesis of ultrafine powders, the majority of them do not allow the production of powder with high specific area and they all generally require a calcination step for the crystallisation of the amorphous phase produced.

Nanocrystalline ceria particles were successfully produced by one-step microwave-assisted synthesis from a glycol solution of metal nitrates under mild conditions (140°C, 1 atm). The as-prepared powder showed a good crystallinity and nanometric particle size. This simple and economic soft chemical method leads to nanometric cerium oxide with an high specific surface area suitable for catalytic applications.

1. Introduction

Cerium oxide is a rare earth oxide that has attracted a great deal of interested owing to its unique properties, such as, oxygen storage capacity and conductivity, high UV absorption and hardness and stability at high temperatures [1]. Because of these characteristics, CeO_2 has been widely used for catalysis [2], fuel cell [3] and sensor [4]. Currently, a number of methods are used to prepare nano-dispersed ceria, including hydrothermal [5], microemulsion [6], precipitation [7] sol–gel [8], and solvothermal synthesis [9]. In most cases however, the powders obtained require an additional calcination step to transform the initial amorphous precursors into a crystalline phase. This process can cause severe aggregation and consequently loss of the nanometric nature of the powders.

Polyol-mediated synthesis, is a simple chemical synthesis that directly precipitates highly pure mixed oxides [10], and a variety of other materials, including sulfides and phosphates, [11] in a high-boiling alcohol. In this procedure, “polyol” stands as a general term for polyalcohols with high boiling temperature and ability to solve inorganic salts. The polyol method is generally applied for the preparation of metal particles mainly for its mild reducing properties. However polyalcohols can also be exploited for their chelating effect that avoids the particles agglomeration during synthesis. In the case of oxide synthesis, the polyol method can than be considered as a sol-gel process carried out at elevated temperatures with an accurate control of particle growth [12]. Due to its high dipole moment, the polyol can also serve as an excellent solvent for microwave heating; microwave-polyol method is in fact a promising method for rapid preparation of nanomaterials. Compared to conventional procedure, microwave dielectric heating has some unique advantages for the synthesis of nanostructured materials: the rapid volumetric heating, causes a fast homogeneous nucleation that in some cases leads to the formation of novel nanostructures.

In this study, a novel method for the preparation of nanocrystalline cerium oxide is reported. Cerium oxide powders were successfully prepared by microwave irradiation under mild conditions (140°C, 1 atm).

2. Experimental

The cerium precursor was dispersed in glycol and the solution was heated in a commercial microwave oven designed for chemical synthesis (MicroSYNTH Plus, Milestone) at the final temperature for 2h. The precipitated powders were separated by centrifugation, washed in ethanol and characterized by X-ray diffraction (Miniflex Rigaku, Japan). The powder morphology was investigated by scanning electron microscopy (SEM, Leica Cambridge Stereoscan 360). The specific surface area was measured by the BET method with the Sorpty 1750 (Carlo Erba).

3. Results and discussion

Nanocrystalline ceria particles were produced by one-step microwave-assisted synthesis from a glycol solution of metal nitrates by adjusting the synthesis conditions.

In particular, the effect of the temperature on the fluoritic phase formation was carrefully studied synthesising powders at four different temperatures between 140 and 180°C. Table 1 summarizes the main characteristics of the samples prepared.

Table 1 – Synthesis temperature, BET specific surface area and crystallite size of CeO_2 samples prepared by microwave irradiation.(*) Measured after calcination at 400°C.

Sample	**MW synthesis temperature (°C)**	**BET surface area* (m^2/g)**	**Crystallite size CeO_2 (nm)**
MW01	180	146	-
MW02	170	167	-
MW03	160	135	6
MW04	140	34	5

The diffractograms of the as-prepared powders (Figure 1) show a drastic effect of the reaction temperature on the nature and numbers of the formed phases. In particular a mix of phases (CeO_2/$Ce(COOH)_3$) is produced for temperatures higher than 160°C, while nanocrystalline pure cerium oxide is obtained at 140°C. This behaviour is probably due to a series of complex redox equilibria involving Ce, NO_3^- and glycol.

The average crystallite size of the as-synthesized powders was estimated by the XRD patterns, using the Debye-Scherrer equation. The average crystallite size of 5-6 nm calculated from the diffractograms was confirmed also by SEM analysis (Figure 2).

The morphologies of the powders synthesized at different temperatures are reported in Figure 3. The pure CeO_2 powders show a spherical shape, while the presence of $Ce(COOH)_3$ as secondary phase induces the formation of more complex morphologies.
A calcination treatment at 400°C is needed both for converting the $Ce(COOH)_3$ into the pure fluoritic phase (samples MW01, MW02 and MW03) and to completely remove the organic residues adsorbed on the surface of all the samples. This heating treatment does not influence the powders morphology indicating that the pure nanocrystalline ceria can be obtained with different morphologies tailoring the $Ce(COOH)_3$/ CeO_2 ratio.
The specific surface area values of the different calcined samples are reported in Table 1. The high surface area (140-170 m2/g) of the samples synthesized at high temperatures (MW01, 02, 03) can be related to the different morphologies induced by the presence of $Ce(COOH)_3$. The micrometric particles of cerium formate that appear at temperatures above 160°C, are transformed into cerium oxides during the calcination step. The CO_2 evolution, associated to this phase conversion, leads to the formation of mesoporous aggregates with high specific surface area retaining the complex morphology (Figure 4). These mesoporous aggregates are suitable for catalytic applications.

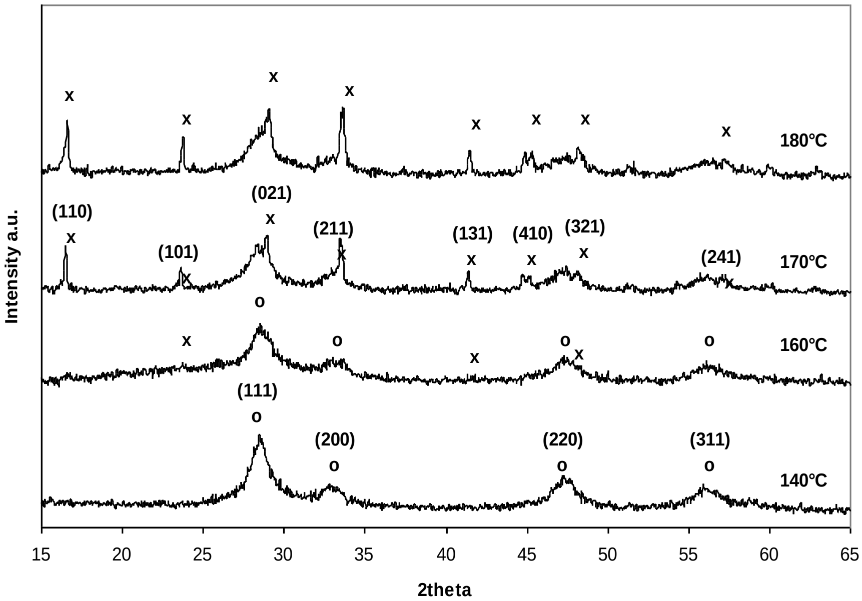

Figure 1 – Influence of the synthesis temperatures on XRD patterns of the as prepared ceria samples. x= $Ce(COOH)_3$, ° = CeO_2.

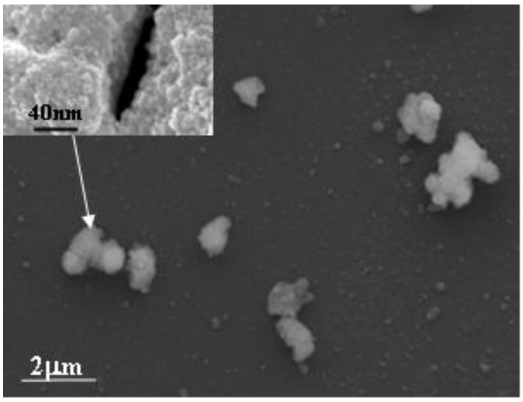

Figure 2 - SEM micrograph of as-prepared ceria at 140°C.

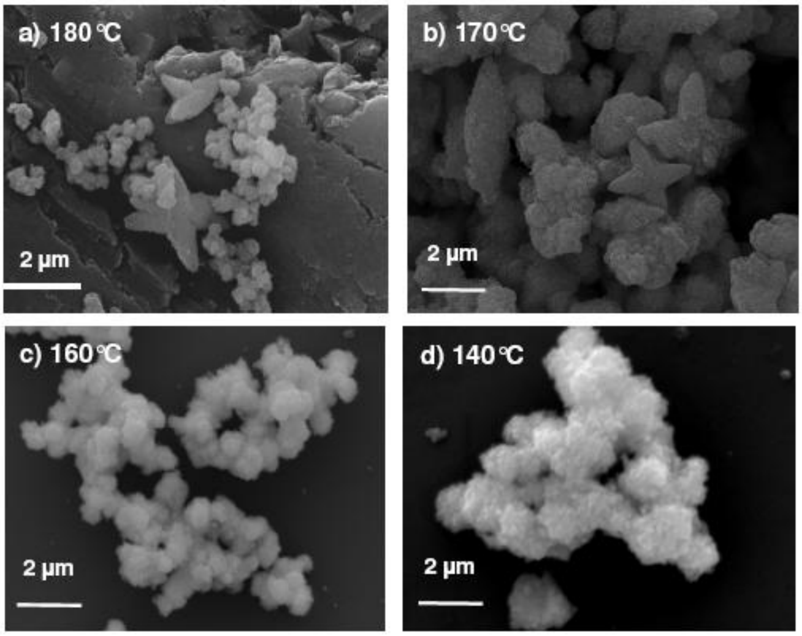

Figure 3 – SEM micrographs of as prepared ceria samples at different temperatures.

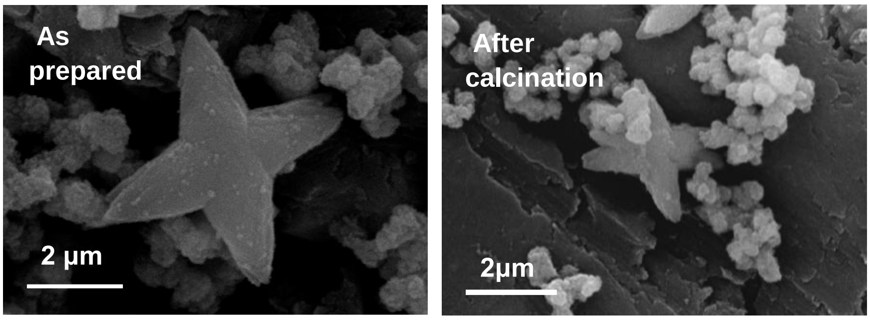

Figure 4 – SEM micrographs of as MW02 before and after calcination.

4. Conclusion

Nanocrystalline ceria particles were successfully produced by one-step microwave-assisted synthesis from a glycol solution of metal nitrates under mild conditions. The as-prepared powder showed a good crystallinity and nanometric particle size. Moreover, by adjusting the synthesis conditions, micrometric nanostructured ceria of complex morphology and high specific surface area can also be obtained.

This simply and economic soft chemical method leads to obtain directly nanometric cerium oxide with an high specific surface area suitable for catalytic applications.

5. References

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