Nanoscale ceria for new functional materials

I V Zagaynov, E A Trusova and V V Belousov
Laboratory of Functional Ceramics, A.A. Baikov Institute of Metallurgy and Materials Science of RAS, Leninskii pr. 49, Moscow, Russia
E-mail: igorscience@gmail.com, trusova@imet.ac.ru

Abstract. Ultra dispersed ceria powders with crystallite size from 10 to 20 nm were synthesized by modified sol-gel and hydrothermal methods using cerium (III) nitrate as source of metal. N,N-dimethyloctylamine, monoethanolamine or tetraethylammonium hydroxide were used as a surfactant in syntheses. It was shown that increase of surfactant/Ce molar ratio value resulted in decreasing dispersion of obtained cerium oxides. It was shown that surfactant nature in the hydrothermal method had no significant effect on the dispersion of ceria obtained. Ceria had mesoporous structure with pore size less than 15 nm.

1. Introduction
Nanostructured inorganic particles are promising systems as oxidation catalysts due to the high surface to volume ratio. Especially, nanoscale ceria containing composites are very attractive three-way catalyst systems for soot combustion reactions [1], SOFC [2], biological applications, solar cells, electrochromic devices, UV radiation filters [3] because of the high mobility of lattice oxygen. The reason for the effect is oxygen donation of ceria caused by partial Ce\(^{4+}\)/Ce\(^{3+}\) reduction on the particle surface [4].

There are many different methods to prepare nanoscale ceria in attempt to optimize its properties for various applications. New techniques have become available due to nanotechnology and have resulted in some progress toward achieving this goal. Several methods were developed for the preparation of CeO\(_2\) nanoparticles, especially such as sol-gel, hydrothermal and microemulsion because they are more promising [5]. We have used sol-gel and hydrothermal methods to establish a correlation between synthesis and thermo treatment conditions from one hand and physical-chemical properties of obtained ceria powders from other hand.

2. Experimental procedure

2.1. Synthesis

- a) sol-gel: cerium (III) nitrate was dissolve in deionized water (0.05M solution) and then after stirring ethanol and a surfactant such as N,N-dimethyloctylamine (DMOA), monoethanolamine (MEA) or tetraethylammonium hydroxide (TEAH) were added, all procedures were carried out at 60-80°C;
- b) hydrothermal: as-prepared sol (as described above) was treatment at 130°C during 3h.

Initial molar ratio value surfactant/Ce in the reaction mixture was changed in the range 1-20. At the final stage of preparation obtained substances were stepwise calcined at 500°C.
2.2. Characterization

The powders prepared by these methods were characterized by X-ray diffraction (XRD) using CuKα radiation (DRON-3M, Russia). Specific surface areas of the catalysts were measured by a conventional (BET) nitrogen sorption method (Tri Star 3000 Micromeritics).

Testing of catalytic activity of obtained ceria powders was carried out in modeling CO oxidation reaction with use the fixed-bed quartz tube reactor at 50-400ºC. The inlet gas composition was 3.8 vol.% CO, 7.3 vol.% O2 and N2 as balance, and the flow rate was adjusted to 30 mL/min (volume rate was 1800 h⁻¹). Analysis of gas reaction products was carried out by gas chromatography (Chrom-5).

3. Results and discussion

Figure 1 shows the typical XRD pattern of the synthesized ceria nanopowder. All reflexes in the XRD pattern were perfectly indexed as the pure cubic phase (Fm3m, JCPDS-34-0394) of CeO2.

According to XRD data calculation by Scherer formula the size of ceria crystallites was ≤20 nm for all samples (table 1).

| №  | Method      | Surfactant | D_{CeO2}, nm |
|----|-------------|------------|--------------|
| 1  | sol-gel     | DMOA       | 12           |
| 2  | sol-gel     | TEAH       | 14.5         |
| 3  | sol-gel     | MEA        | 21           |
| 4  | hydrothermal| DMOA       | 12           |
| 5  | hydrothermal| TEAH       | 11           |
| 6  | hydrothermal| MEA        | 12           |

It was found that with increasing molar ratio of DMOA/Ce from 1 to 20 the crystallite size dependence of this ratio is nonlinear (figure 2a). The minimum crystallite size of 12 nm was observed at DMOA/Ce=1.

The comparison of ceria dispersibility was carried out for powders obtained by use of different surfactant in sol-gel synthesis at the molar ratio value surfactant/Ce = 1. It is possible that smaller crystallite size (12 nm) and highest BET surface (figure 2b) were achieved due to the presence of relatively long hydrocarbon chain in the DMOA molecule. The analysis of figure 2b also shows that the use of TEAH and MEA as surfactant results in larger CeO2 particles. It is interesting that using of TEAH instead of DMOA ceria particle size increased slightly (~20%), however, the BET surface value reduced by more than 30%. Replacing of DMOA by MEA leads to doubling of ceria crystallite size and at the same time to reduce BET surface value almost 4 times. Apparently, the steric hindrance caused by DMOA and TEAH presence in the reaction mixture prevented the formation of larger crystallites. In addition the availability of long hydrocarbon chain in DMOA molecule promotes the formation of a more developed surface than the availability of TEAH or MEA, but the use of MEA resulted in a more narrow distribution of pores than the use of TEAH or DMOA (figure 3).

In the case of hydrothermal method when molar ratio surfactant/Ce value was 1 the crystallite size was almost the same (about 11-12 nm) for all surfactants (table 1). The all obtained ceria samples had mesoporous structure.

Ceria powders were tested in model CO oxidation reaction. It was shown that the onset temperatures (CO conversion was 10-15%) for all catalysts were in the interval 100-180°C, at temperatures 350-370°C CO conversion reached 100% (table 2).
Figure 2. Impact the amount (a) and type (surfactant/Ce=1) (b) of surfactants on the average crystallite size (D) and surface area (S) of ceria powders obtained by sol-gel technique.

Figure 3. Mesoporous (a) and micro-mesoporous (b) structures of obtained ceria powders (number 3 and 2 according to table 1).

Table 2. Reaction conditions and catalytic activity of CeO₂ obtained by sol-gel technique.

| №  | Surfactant | Surfactant/Ce | T₂₅%, °C | T₅₀%, °C | T₉₉%, °C |
|----|------------|---------------|----------|----------|----------|
| 1  | DMOA       | 1             | 220       | 260      | 348      |
| 2  | DMOA       | 5             | 238       | 267      | 363      |
| 3  | DMOA       | 10            | 260       | 285      | 358      |
| 4  | DMOA       | 20            | 203       | 240      | 347      |
| 5  | TEAH       | 1             | 195       | 250      | 333      |
| 6* | MEA        | 1             | 253       | 290      | 397      |

volume rate was 1800 h⁻¹ and *5000 h⁻¹
4. Conclusion

The family of nanoscale ceria powders with average crystallite size less 20 nm was obtained by sol-gel and hydrothermal methods. All synthesized powders have mesoporous or micro-mesoporous structure with pore size not exceeding 15 nm. It was found that with increasing molar ratio DMOA/Ce value from 1 to 20 the crystallite size and specific surface area dependences of this ratio are nonlinear and have the upper and the lower extremes, accordingly, on their curves.

It was shown that the hydrocarbon chain length and three-dimensional configuration of surfactants using the sol-gel synthesis affects the dispersion and specific surface of ceria obtained. Contrary to using the hydrothermal method, nature of N-containing surfactants has no significant effect on the dispersion of ceria obtained, and its particle size reached low values.

References

[1] Blanco G, Calvino J J et al. 1999 Chem. Mater. 11 3610
[2] Milliken Ch, Guruswamy S, Khandkar A 2002 J. Am. Ceram. Soc. 85 2479
[3] Eliseev A A , Lukashin A V 2010 Functional Nanomaterials (Moscow: Physmatlit)
[4] Kockrick E, Schrage Ch, Grigas A, Geiger D, Kaskel St 2008 J. Solid State Chem. 181 1614
[5] Ivanov V K, Polezhaeva O S, Tret’yakov Yu D 2010 Russ. J. Gen. Chem. 80 604
[6] Zagainov I V, Trusova E A 2010 Composites based on mesoporous aluminium-silicates: synthesis by sol-gel method and physical-chemical properties III International Competition of Scientific Papers in Nanotechnology for Young Researchers (Moscow, Russia, 1-3 November 2010) s.5 № 22

Acknowledgments

This work was supported by grant RFBR № 09-08-00917-a, Program of Basic Research № 22 of the Presidium of RAS, and Program of Department of Chemistry and Materials Sciences № 7 of RAS.