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Review

Synthesis and Specific Properties of the Ceria and Ceria-Zirconia Nanocrystals and Their Aggregates Showing Outstanding Catalytic Activity in Redox Reactions—A Review

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Abstract: Non-stoichiometric CeO$_{2-y}$, especially in the form of nanocrystal aggregates, exhibits exceptional catalytic activity in redox reactions. It significantly improves the activity of transition metals and their oxides dispersed on/or in it, also acting as an oxygen buffer. Particularly, active oxygen species (O$_2^{n-}$, O$^-$) are generated at the M/CeO$_{2-y}$ nanoparticle interface, as well as in the surface layer of their solid-state solutions M$_x$Ce$_{1-x}$O$_{2-y}$. The crystal structure of CeO$_2$, ZrO$_2$ and (Ce, Zr)O$_2$ and its defects are discussed in connection with the resulting specific catalytic activity. All the methods (simple precipitation and co-precipitation from mother liquors, sol–gel methods, precipitation from nanoemulsions, hydrothermal and solvothermal techniques, combustion and flame spray pyrolysis, precipitation using molecular and solid-state matrices, 3D printing and mechanochemical methods) used for the synthesis of these nanomaterials are comprehensively reviewed, describing the rules of individual procedures and preparation details. Methods of deposition of metal catalysts and their oxides on CeO$_2$ nanoparticles, such as impregnation, washcoating and precipitation deposition, were also discussed. This review contains more than 160 references to representative papers wherein the reader can find further details on individual syntheses of effective ceria-based catalysts for redox reactions.

Keywords: ceria nanoparticle synthesis; ceria nanoparticle structure; ceria-based catalyst specificity; oxygen storage capacity

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1. Introduction

A desired property of most catalyst carriers is ability to form high-surface-area materials with appropriate porous structure, e.g., mesoporous or hierarchical, on which high-surface-area catalytic precursors are dispersed. During subsequent chemical and temperature treatments, these precursors are transformed into embedded nanoparticles with active sites for a given catalytic reaction. During these treatments and subsequent treatments as a catalyst, these nanoparticles should not be sintered, thereby losing active sites. In addition, the porous structure of catalytic carriers should provide reactants with easy access to the active sites on the inner pore walls, as well as easy diffusion of the reaction products back to the gas phase.

The nanocrystal aggregates of CeO$_{2-y}$, or solid-state solutions Ce$_{1-z}$Zr$_z$O$_{2-y}$, or mixed oxides CeO$_2$-ZrO$_2$ obtained in the developed synthesis methods show mesoporous [1–5] and hierarchical [6–8] structures satisfactorily meeting these requirements. Sometimes, mesoporous ceria-based catalysts M$_x$Ce$_{1-x}$O$_{2-y}$ are obtained in a single step, for example, using reverse nanoemulsion methods [9–15].

Moreover, these nanocrystals exhibit catalytic activity in redox reactions and even in cases of noble metals or transition metal oxides dispersed on these ceria-based aggregates, lattice oxygen and oxygen vacancies of the ceria lattice can participate in one or more steps of the catalytic circle proceeding with these complex catalysts [3,14,16–18]. These active catalytic supports can also help in gasification of carbon deposits poisoning oxidation or reforming catalysts (especially dry reforming) of organic compounds [18–21]. CeO_{2-x} additives also help to reactivate diesel filters by oxidizing carbonaceous deposits that build up during engine operation [22]. Such catalytic activity is expressed in the ability to donate oxygen under reducing conditions and take it back under oxidizing conditions [3,23–25]. The limited changes in the stoichiometry caused by this participation usually do not cause changes in the essential fluorite-type structure of CeO_2 and $Zr_zCe_{1-z}O_{2-y}$ until z = 0.2, although as z increases, more and more deformation occurs in CeO_6 octahedrons [26]. However, the progress of the reduction can change nanocrystal face exposures [27–29].

Another important feature of CeO_2 is the ability to incorporate various active transition metal ions, creating solid solutions $M_xCe_{1-x}O_{2-y}$ within quite wide limits of x [1,3–5,11,24,30,31]. Such systems are characterized by both the variability of the M and Ce oxidation number and the concentration of anion vacancies and even the possibility of forming particularly active oxygen species, peroxides ${O_2}^{2-}$ and superoxides ${O_2}^{-}$ [3,14,17,32,33]. Experimental evidence for the involvement of these active oxygen species using near-ambient-pressure XPS (NAP-XPS) has been compiled in a monograph written by Llorca's research group [34].

Therefore, the characterization of ceria-based catalysts usually includes the measurement of the oxygen storage capacity (OSC) [3,5,14,15,17]. Exceptionally high OSC values allow ceria-based catalysts to maintain the stationarity of catalyzed reactions during their operation; they act as an oxygen buffer. This is supplemented by exceptionally high oxygen mobility owing to the fast oxygen transport pathways in defected CeO_{2-y}, $Ce_{1-z}Zr_zO_{2-y}$, $M_xCe_{1-x}O_{2-y}$ and $M_xCe_{1-x-z}Zr_zO_{2-y}$ crystal lattices, so they are used as a solid electrolyte in high-temperature fuel cells [35–37]. These pathways are most probably used in the generally accepted Mars–van Krevellen mechanism of catalytic redox reactions over ceria-based catalysts [3,17,38–40]. The fast oxygen transport pathways enable using oxygen and oxygen vacancies not only from the superficial layer but also from the deeper layers of the catalysts [41]. This explains the exceptionally high values of OCS in ceria-based catalysts.

The OSC is most often measured by temperature-programmed reduction and oxidation (TPR and TPO) or by isothermal titration with probe molecules (H_2, CO, O_2, N_2O) [42–46]. Ceria-based catalysts with a particularly high OSC are used in processes characterized by rapid and large changes in the redox potential of reaction mixtures, primarily in car catalysts. These catalysts typically contain precious metals (Pt, Pd, Rh) embedded on a ceria-zirconia carrier that covers the surfaces of a metal mesh or cordierite ceramic support to provide good gas flow. An extensive review of this type of catalyst has been presented by Reddy's research group [47]. High OSC is also helpful in inhibiting deactivation of catalysts owing to deposition of inactive carbon deposits [20,48,49] or, in cases of excess depth, reduction of metal ions during catalyst activation or operation [50,51].

The listed features of these ceria-based catalysts mean that they are very often used in green chemistry processes, limiting the harmful anthropogenic impact on the environment. They are commonly used to neutralize exhaust gases from vehicles with combustion engines or from power plants and combined heat and power plants. In many processes of chemical technology, harmful by-products are generated, e.g., volatile organic compounds, which must be incinerated. Here, the crystal and porous structure of ceria-based nanomaterials, methods of their preparation and their specific properties are presented.

Although there are reviews on ceria-based catalysts, there seems to be no one that covers a review of all the methods used to obtain these cerium oxide-based nanomaterials. The aim of our review is not only to fill this gap, but also to link particular methods of synthesis of nanocrystals and their aggregates with their specific crystal structure, their defects and catalytic activity in redox reactions. This review contains many references to original papers, allowing the reader to become acquainted with the details of particular methods of synthesizing ceria-based nanocatalysts and their application in exemplary reactions.

2. Concise Description of the Crystal Structure of CeO_{2-y}, ZrO_{2-y} and $Zr_zCe_{1-z}O_{2-y}$

Crystal structures, their defects, phase transitions and the phase diagrams of CeO_{2-y}, ZrO_{2-y} and $Zr_xCe_{1-x}O_{2-y}$ systems were reviewed in detail by Yashima [26]. In the phase diagram of CeO_{2-y} within $0 < y < 0.5$, at least six phases were recognized which differ in molar ratio O:Ce and in space groups from fluorite-type to triclinic. The closer the ratio O:Ce is to 2:1, the more likely it is there is only the fluorite phase. The cubic fluorite structure of CeO_2 belonging to the space group Fm3m is formed of CeO_6 octahedrons and OCe_4 tetrahedrons. Normally, ceria preparations show some kind of oxygen deficit, i.e., oxygen vacancies, which is compensated by partial reduction of Ce^{4+} to Ce^{3+}. The last ion has a radius about 15% larger, which corresponds to an approximately 50% larger volume than Ce^{3+}. An increase in lattice parameters with the reduction of ceria can be observed even in case of solid solutions $M_xCe_{1-x}O_{2-y}$ despite the formation of oxygen vacancies at the same time [11,13]. The most common impurity of the CeO_2 fluorite phase is the $Ce_{11}O_{20}$ phase belonging to the P1 group [52]. This phase is characterized by a 30% formal reduction of Ce^{4+} to Ce^{3+} and 15% concentration of oxygen vacancies.

An increase in temperature intensifies the vibrations of Ce-O bonds anisotropically in the {111} direction, as was shown in calculated electron density maps [53]. These vibrations cause deformation of the polyhedrons, which in combination with the already existing anion vacancies creates two pathways of easy diffusion of oxide anions in the {111} direction and the z axis.

Zirconia (IV) oxide shows three clear phase transitions but at high temperatures that do not occur in catalytic processes. According to Yashima and Mitsuhashi [54], the first-order martensitic transformation from the monoclinic to the tetragonal phase only occurs at 1400 K and is characterized by high hysteresis. The monoclinic phase of ZrO_2 shows baddeleyite structure ($P2_1/c$), which can be described as such a strongly deformed fluorite structure for which the coordination number of zirconium (CN_{Zr}) is equal to 7. The tetragonal zirconia phase ($P4_2/mcm$) can be imagined as a little less deformed fluorite structure with $CN_{Zr} = 8$. At a very high temperature (2642 K), this tetragonal phase is transformed into the real cubic fluorite structure with $CN_{Zr} = 6$.

A common addition to CeO_2 is ZrO_2; this oxide itself is thermally much more stable which improves the thermal stability of $M_x(ZrCe)_{1-x}O_{2-y}$ materials in relation to $M_xCe_{1-x}O_{2-y}$. This is owing to the fact that $M/(ZrCe)_{1-x}O_{2-y}$ and $M_x(ZrCe)_{1-x}O_{2-y}$ catalysts can be applied in high-temperature processes, e.g., in the exhaust systems of vehicles, which is discussed in detail in a review published by Reddy's group [47]. Numerous research papers by Yashima's team, cited in [54], allow one to accurately determine the phase diagram of $Zr_zCe_{1-z}O_2$ within a wide range of z. Within $1 \leq z \leq 0.92$, there is a single monoclinic phase of ZrO_2. Within the next narrow range of $0.92 \leq z \leq 0.88$, an admixture of tetragonal ZrO_2 occurs, for which the t phase above $z = 0.88$ is present only up to $z = 0.80$. Above this value of z, namely within $0.80 \leq z \leq 0.40$, only the next tetragonal phase t' exists. Within $0.40 \leq z \leq 0.35$, the concentration of the third tetragonal phase t'' gradually increases. With further increases in Ce concentration, only one tetragonal phase t'' exists up to $z = 0.10$. Below this value of z, only the ceria cubic phase exists in the system. In a later study, Yashima [55], using high-angle X-ray diffraction, showed that the size of the crystalline $Zr_zCe_{1-z}O_2$ system can change the range of existence of these t phases.

Although the mobility of anions in zirconia lattices is much lower than in the ceria lattice, even a small addition of Zr to the ceria lattice improves the anion mobility [56]. This is due to the deformation of the cubic structure of ceria in the direction of pseudo-cubic or pseudo-tetragonal structure where $z > 0.1$. This involves a slight shift of the O ions towards their position in the tetragonal lattice while the Ce and Zr ions remain in the positions of the cubic lattice. This deformation, impossible to notice in standard powder XRD, was observed in Raman spectroscopy and EXAFS by Yashima and Morimoto [57] and confirmed later using the same spectroscopic analyses by Vlaic for Rh-$Zr_zCe_{1-z}O_2$ catalysts [58].

The DFT calculation performed on the super cell Ce_8O_{16} of the fluorite structure showed that gradual atom-by-atom removal of oxygen causes lengthening of some—and shortening of other—Ce-O bonds, thus creating pathways of the fast diffusion of oxygen [59]. A similar calculation on the Zr_8O_{16} super cell of tetragonal structure showed an analogue formation of the fast diffusion pathways with advance of gradual removal of oxygen atoms [53]. The experimental measurements of oxygen diffusion as a function of the $Zr_zCe_{1-z}O_2$ system's composition showed the highest oxygen mobility for equimolar composition $Zr_{0.5}Ce_{0.5}O_2$ [56] which was in accordance with prediction coming from the calculated maximum of the molecular entropy in the $Zr_zCe_{1-z}O_2$ system [60]. The results of the neutron diffraction measurements showed a shift of oxygen atoms in the {111} direction which creates pathways for the fast oxygen diffusion in {100} and {110} directions [61].

Surface reduction of ceria nanocrystals may change termination faces between (001), (110) and (111) [27,29]. Differences in reducibility of individual crystal faces of CeO_2, (001), (110) and (111) have been investigated by Yuan and Haile and related to differences in the surface concentration of Ce^{3+} [29]. Such differences in the reduction of different faces were also observed during etching of ceria nanocrystals in liquid cell TEM [62]. Surface reduction may take place during thermal aging used to activate the ceria-based catalysts, causing structural changes at least in their surface layers [63]. Re-faceting of the exposed surface of ceria-based nanocatalysts may also occur during catalyzed reactions, especially of the redox type [27,28]. A mechanism for such surface re-faceting has been proposed by Yang et al. [64]. As was shown by Montini [65] during the deep reduction of the equimolar oxide system ZrO_2-CeO_2, a new phase $Ce_2Zr_2O_{7+x}$ appears of pyrochlore structure $(Na,Ca)_2Nb_2O_5(OH,F)$. The $Ce_2Zr_2O_{7+x}$ phase may be presented as a pseudo-cubic one where cations are located at corners and centers of the cube's faces and seven oxygen ions are stochastic located at the tetrahedrons positions. This phase undergoes reversible redox cycles within a wide range of x.

In search of fast conductors of oxygen ions, the cubic cerium oxide systems containing admixtures of the rare metal R were frequently investigated. It was found that, in all cases, conductivity occurs through the hopping of O ions to adjacent anion vacancies and the highest conductivity occurred for composition $R_{0.2}Ce_{0.8}O_{1.9}$ [56]. Among rare earth elements, the highest conductivity was shown for addition of Gd and Sm. However, in case of Y admixtures, the conductivity maximum occurred for a different composition, i.e., $Y_{0.07}Ce_{0.93}O_{2-y}$ [66]. Studies of electrical conductivity and impedance spectroscopy showed that the conductivity of $Cu_xCe_{1-x}O_{2-y}$ solid solutions increased with Cu doping and is both electronic and ionic [67]. It has been shown that the catalytic activity in the total combustion of volatile organic compounds (VOCs) depends mainly on oxygen ions' conductivity and the ion-hopping mechanisms of this conductivity have been confirmed.

3. Synthesis of the Ceria-Based Nanoparticles

Nanomaterials are usually defined as materials composed of nanoparticles with at least one dimension $d < 100$ nm. They are characterized by a significantly increased number of atoms located on the surface in relation to those located in the bulk of materials. In the case of nanocrystalline nanomaterials, less stable faces and atoms or ions located on the edges and vertices of intersecting faces are exposed in greater numbers. In these sites, atoms or ions appear that are significantly unsaturated in valence and, thus, predestined to be active sites of catalytic reactions. Xie et al. [68] showed this for the intersection of nanocrystal facets (111) and (002) of CuO/CeO_2 nanocrystals obtained by the hydrothermal method (described later). The highest concentration of oxygen vacancies was also close to these intersections. Surface and volumetric structural and chemical defects should be added here. In the case of CeO_2-based nanocrystals, oxygen vacancies and reduced Ce^{3+} ions play an important role [14,69]. This role may also be played by surface defects; in the case of CeO_{2-y}, they are oxygen vacancies and reduced Ce ions. Therefore, partially reduced nanometric ceria mesoporous systems with a large specific surface area are catalytically valuable.

Methods of obtaining such nanomaterials can be divided generally into chemical and mechanochemical methods. Chemical methods are usually performed in two stages. During the first stage, a nanometric carrier CeO_{2-y} or $Zr_xCe_{1-x}O_{2-y}$ is obtained. Such carriers already have their own catalytic activity. In the second stage, precursors of noble metals or transition metal oxides are deposited on the ceria-based carrier obtained previously. Mechanochemical methods are usually single-step, although it is not uncommon for additional fragmentation of nanomaterial agglomerates to be necessary.

The simplest of the chemical methods to obtain CeO_{2-y} or $Zr_xCe_{1-x}O_{2-y}$ nanoparticles is precipitation or, respectively, co-precipitation of hydroxide and/or hydroxyoxide aggregates by a carefully controlled addition of a pH-raising agent to a solution of ceria nitrates or chlorides, usually. After some time of maturation of these aggregates, they are separated by centrifugation from the saturated mother liquors and washed, dried and calcined, to produce ceria carriers. In the case of co-precipitation, the precipitates of the metal ions used must have comparable solubility products. By manipulating the parameters of precipitation and subsequent operations, materials with the desired nanometric particle size can be achieved. They may, however, turn out to be phase-inhomogeneous. An example is the flower-shaped $Cu_zZr_xCe_{1-x-z}O_{2-y}$ catalyst which contains a cerium-enriched cubic phase and a zirconium-enriched tetragonal phase [70]. Nevertheless, these biphase catalysts, also called mixed oxides, were satisfactorily active in the preferential oxidation of CO.

Optimization of cerium concentration, anion type, pH values, process temperature and time can lead to obtaining nanoparticles of the desired shape. The driving forces here are the structural anisotropy of the chemical compound and the chemical potential of the mother liquor. For example, Mai [71] used the high asymmetry of Ce(III) hydroxide in the precipitate to produce CeO_2 nanorods after drying and calcining. It was necessary to add concentrated (6–9 M) NaOH to the $Ce(NO_3)_3 \cdot 6H_2O$ solution to accelerate the precipitation of $Ce(OH)_3$ nuclei. Less concentrated solutions and increased temperature finally resulted in CeO_2 nanocubes. However, Wu et al. [72] and Wang et al. [73] reported that chloride ions interacting on the (111) and (100) faces of growing crystals cause increases in the proportion of nanowires and nanorods (1D growth preferred), while NO_3^- anions favor the formation of nanocubes.

It would seem that these various statements can be explained by the results of the study by Liu et al. [74]. These authors observed that starting with cerium(III) nitrate or chloride in both cases yielded nanorods growing in the {111} direction. The differences are manifested in the exposure of the faces: (100) and (110) for nitrates and (111) and (100) for chlorides. However, this is not a certain rule because, by doing the same, Agarwal et al. [75] found only sidewall exposures (111). Therefore, there are reports of various shapes of terminal faces of nanorods, most often hexagonal, pentagonal and rectangular. The influence of the anions used in the synthesis on the shape of the obtained crystallites and their aggregates is not unambiguous, because the other factors affecting it are mutually intertwined. Therefore, there are still publications focused on this problem [76–79].

Taking into account the crystal structure of CeO_2, the most stable structure of its nanocrystals should be in the shape of octahedron. However, it is often not thermodynamics that determines the shape of growing nanocrystals, but the kinetics of this growth. Then, octahedral crystals with truncated corners (tetradekaedrons) are formed as well as other less symmetrical crystal shapes. Therefore, apart from faces belonging to the (111) family, facets belonging to other face families are also displayed.

Crystal growth can be controlled by the addition of various inorganic and organic substances. For example, Zhang et al. [80] showed that a small addition of decanoic acid, which preferentially binds to (100) facets, inhibited the growth of nanocrystals in the {100} direction and accelerated in the {111} direction, resulting in the formation of nanocubes. However, larger additions of this acid also inhibit the growth in the {111} direction, thus causing the formation of smaller nanoparticles in the shape of octahedrons with truncated corners. It should be added that the frequent structural defects in nanorods make it difficult to unambiguously interpret their exact morphology. Recently, it was possible to control the ratio of exposed faces (111)/(110) in nanometric cup-shaped CeO_2 particles [81].

It is also possible to force the desired shape of ceria nanoparticles, e.g., in the form of nano-needles, by adding Al^{3+} ions introduced into the CeO_2 network [82]. In turn, the introduction of Eu ions promoted the growth of $Eu_xCe_{1-x}O_2$ nano-cups ($x < 0.4$), while improving the redox activity [83]. In the range of higher Eu concentrations ($x > 0.4$), the formation of ordered defect structures was observed. It has also been shown that the presence of water on the surface of CeO_2 nanoparticles affects the evolution of their shape [84]. Xie et al. [68] prepared a series of CuO/CeO_2 nanocatalysts with octahedron, rod, cube, sphere and spindle morphologies. The highest activity in CO oxidation was found for intersection of nanocrystals planes and, among them, the highest concentration of oxygen vacancies showed intersection of (111) and (002) facets.

Ceria as a semiconductor can be doped by aliovalent cations and anions in relation to the Ce^{4+} and O^{2-} ions causing redox changes of these ions, generating point, geometric and chemical defects, changing the electrical conductivity and also creating active sites for catalytic reactions [85]. In case of the doped CeO_2-based catalysts, anion vacancies, redox pair Ce^{4+}/Ce^{3+} and transition metal single-ion sites $M^{n+/(n-1)+}$ are generated [12]. All of them, depending on the reaction, may take place in the catalytic circle. Cop et al. [15] tried doping mesoporous CeO_2 with both isovalent Zr and aliovalent Gd, Pr and Tb ions to optimize catalytic activity in the HCl oxidation reaction. There are reports on changing the shape of growing crystals of CeO_2 caused by different doping methods with metal ions [77].

In addition, changes in the shape and exposure of the walls may arise at the calcination stage. Ta et al. [86] observed a change in the exposure of walls (110) and (100) to (111) after increasing the calcination temperature from 400 to 700 °C. Bezkrovnyi et al. [87] observed temperature-activated reconstruction of CeO_2 nanocubes into a zig-zag structure of (111) nanofacets which increased the catalytic activity in CO oxidation.

Also, the reactants of catalyzed reactions may cause structural changes in the CeO_2 lattice as was showed by Yang et al. [88]. These authors, using CO adsorption (IRRAS) and HRTEM on single crystals with exposed (111) and (110) faces, observed the reconstruction of a large part of the (110) faces into (111) faces. Matsukawa et al. [26] noticed a structural transition of CeO_2 with increasing temperature in the presence of hydrogen related to partial bulk reduction of CeO_2. Wang et al. [63] studied the activating effect of elevated annealing temperature on the formation of active sites in Cu/CeO_2 catalysts. Yuan and Haile [29] noticed a strong dependence of the surface reduction progress on the type of exposed walls, i.e., (001) and (110) or (111). Polo-Garzon et al. [28] described and discussed this surface reconstruction for various metal oxides and its influences on their catalytic activity. Recently, Yang et al. [64] proposed a mechanism of surface re-faceting in cubic ceria nanocrystals.

Llorca's group observed the reorganization of bimetallic nanoparticles caused by the catalytic reaction taking place on them [89]. These were RhPd particles deposited on ceria nanocubes and nanorods on which steam reforming of ethanol was carried out. The dynamics of this reorganization depended on the type of exposed ceria face. Li et al. [90] investigated the effect of the shape of CeO_2 nanoparticles on the surface diffusion of Ru deposited on them. Liu et al. [91] observed that 2 nm NiO nanoparticles deposited on the (111) face of CeO_2 at 500 K and in contact with CH_4 migrate and form solid solutions $Ni_xCe_{1-x+}O_{2-y}$. Liu et al. [92] noticed that the formation of alloys between metallic Ni and Cu nanoparticles deposited on a CeO_2 support clearly depends on the morphology of the support used. Wang et al. [93] investigated the structural stability of various CeO_2 structures during catalytic steam reforming of ethanol on Ir/CeO_2 nanocatalysts. Differences in sintering of Au nanoparticles on flat faces (100) and (111) and on zig-zag nanofacetted structures on (111) faces were also observed [94]. These differences were related to differences in the preferential oxidation of CO. This is related to the direct observation by Sung et al. [62], namely an increased redox sensitivity of nanofacets on nanocrystalline ceria revealed during etching in liquid cell transmission electron microscopy. During CO oxidation over doped ceria nanocatalysts, Sartoretti et al. [95] observed evolution of defects in these nanocatalysts using in situ Raman spectroscopy.

The use of urea as a precipitating agent, which, when added to a solution of cerium-zirconium salts and hydrolyzed at a temperature close to the boiling point of the solution, leads to the precipitation of mixed hydroxyoxide with gelling additives, was described in US patents [96,97]. The next steps were thermal maturation of the gel and removal of water from the gel with a solvent with a low surface tension, e.g., dry 2-isopropanol, after which the material was dried and calcined in a flow of dry air or a suitable mixture containing Ar, O_2 and CO_2. Finally, mixed oxides of $x(ZrO_2){\cdot}(1-x)CeO_2$ nanocrystals with a size of 4–9 nm and their aggregates of 100–1000 nm were produced. Other descriptions of such carriers' precipitation with urea can be found, for example, in [98,99]. Wolski, et al. [100] compared the catalytic activity of Au-CeO_2 nanocomposites co-precipitated rapidly from mixed nitrates by the addition of NaOH with catalysts co-precipitated slowly after addition of hydrolyzed urea or hexamethylenetetramine. The rapidly precipitated nanoparticles were finer, more homogeneous in size and more active in low-temperature oxidation of benzyl alcohol. Mileva et al. [101] obtained a mesoporous Ti-Ce oxide nanomaterial using co-precipitation with urea. It was found that the Ti:Ce ratio determined catalytic activity in the methanol decomposition and ethyl acetate oxidation.

Nanometric CeO_{2-y} and $Zr_xCe_{1-x}O_{2-y}$ mixed oxides with a specific surface area of up to about 130 m^2/g are also obtained by the sol–gel method, i.e., modified Pechini method [102], originally designed for obtaining ceramic dielectrics. It starts with the preparation of a colloidal hydroxy-alkoxy sol, in which metal ions are dispersed, forming a gel [103]. Colloidal products are usually extracted in ultracentrifuges and, as pointed out by Li et al. [104], the large differences in density produced by them determine which colloidal nanostructures are separated, and this determines what the products of further processing will be. Properly applied slow drying and annealing leads to the removal of alkoxyl and hydroxyl ions, converting the material into a nanometric oxide or mixed oxide. The parameters that must be controlled during the process are the pH and stoichiometry of the solution, the amount of water added during hydrolysis, gel time, temperature and effective solvent removal [105]. It is assumed that the structure of the obtained gels is amorphous and only the maturation stage leads to the formation of a crystalline structure.

The use of surfactants significantly increases the surface area of these materials, but it relates to the complication and extension of the synthesis time due to the need to wash out the organic compounds with a mixture of water and acetone. Terrible [106] obtained cerium-zirconium oxide nanomaterials with a surface area of up to 235 m^2/g using cetyltrimethylammonium bromide as a surfactant. The final materials were composed of nanoparticles (4–6 nm) and were highly porous (0.66 cm^3/g). Recently, Chavhan, et al. [107] prepared CeO_2 nanoparticles via a modified hydrothermal method using urea and NaOH. A structure-directing surfactant agent cetyltrimethylammonium bromide (CTAB) was applied to force growth from spherical to irregular polygonal morphology. The initial 18–20 ceria nanocubes after hydrothermal reaction exposed highly reactive (100) faces. Addition of CTAB caused a reduction in the size of CeO_2 to 8–10 nm with the (111) exposition of these more stable (111) faces; at the same time, concentrations of oxygen vacancies and Ce^{3+} were enhanced in the cubic fluorite structure. This CeO_2 nanomaterial obtained using the prompt procedure showed increasing structural disorder in the following order: nanocubes < nanoplates < polygonal structures < nanospheres. On the surface of CeO_{2-y} and $Zr_xCe_{1-x}O_{2-y}$ nanoparticles obtained after the completion of the first stage of catalyst synthesis, i.e., after their calcination, noble and transition metals are deposited in the second stage of this synthesis. The simplest method is impregnation of these carriers with a solution containing salts or complexes of the catalytically active metals mentioned. After drying and thermal and chemical treatment, they remain as metal or metal oxide film covering the surface of the ceria-based support. An example may be CuO/CeO_2 catalysts obtained by the wetness incipient impregnation method using a solution of $Cu(NO_3)_2$ and nanoparticles of CeO_{2-y} [67]. These catalysts were significantly less active in catalytic incineration of VOCs than nanocrystalline solid solutions $Cu_xCe_{1-x}O_{2-y}$ with the same Cu:Ce atomic ratio.

By using more advanced methods of covering nanoparticles with nanocrystals of another oxide, i.e., by decorating these nanoparticles, a material with a different, or even higher, catalytic activity is obtained than when implementing the component oxides separately. In our laboratory, we obtained nanocatalysts CeO_2/Mn_3O_4 and CeO_2/Co_3O_4 with a molar ratio Ce:M = 1:99 using the deposition precipitation method described below [3,5]. Although the 10–15 nm nanoparticles of Mn_3O_4 and Co_3O_4 were very active, decorating their surface with 2–5 nm CeO_{2-y} nanocrystals (which were much less active separately) resulted in a significant increase in the catalytic activity in the oxidation of VOCs. Another example, reported by Huang et al. [17], is the synthesis of nanocrystalline CeO_{2-y} decorated with β-MnO_2 nanorods. These catalysts were distinguished by an increased oxygen transfer capacity, which is crucial for the activity of oxidation reaction catalysts using the Mars–van Krevellen mechanism. Mori et al. [108] obtained CoO_x-decorated CeO_2 heterostructures and noticed the dependence of catalytic activity in diesel soot combustion on the morphology of these catalysts.

Similarly, Liu et al. [92] prepared multi-metallic catalysts on different shaped CeO_{2-y} using an impregnation method. They revealed dependence of Ni-Cu alloying behavior on the support morphology. Only the nanopolyhedron ceria made it possible to obtain homogeneous nanoalloys owing to the equivalent interactions of Ni and Cu species with CeO_{2-y} (111) facets exposed on the nanopolyhedrons of CeO_2. Such catalysts showed outstanding catalytic performance in acetylene and hexyne hydrogenation, confirming the importance of the proper tailoring of the support morphology.

Other modifications of simple impregnation have also been used to improve the uniform dispersion of deposited nanoparticles. Before impregnation of the cerium supports with an ammonia solution of tetraammineplatinum(II) in 2-propanol, they were pre-treated for several hours with organic acids (maleic or citric) [96]. Similarly, using a modified impregnation method, a WO_3-$TiO_2/Zr_xCe_{1-x}O_2$ catalyst was obtained and successfully used in the selective catalytic reduction of NO_x with ammonia (NH_3-SCR) process with mixtures imitating the composition of exhaust gases from diesel engines [109]. Di Sarli et al. [22] applied a wash-coated diesel particulate filter (DPF) with highly dispersed nanometric CeO_2. This filter allowed for total removal of the soot covering the filter starting from 475 °C and remaining stable for multiple coating and soot removal cycles. These authors [49] also compared the activity of SiC DPFs pre-coated with cerium oxide and then wash-coated with Cu and Ag nitrates with filters wash-coated with a suspension of nanometric CeO_2 in metal nitrate solution. By far, the best catalyst for soot removal turned out to be the Ag-promoted DPF obtained by the second procedure, similar to the deposition–precipitation method.

The deposition–precipitation method consists in preparing a suspension of fine particles of a high-surface-area carrier, e.g., CeO_{2-y}, to which a solution containing catalytically active transition metal salts is added. Then, a precipitating agent, e.g., ammonia solution, is gradually added dropwise, causing precipitation and deposition of hydroxyoxides on the surface of the carrier. After centrifugation of the solids, washing, drying and calcination, the active ingredient is highly dispersed on the surface of the carrier. Examples are a series of cerium-zirconium catalysts deposited with an NH_3 solution on aluminum, titanium and silicon oxides that have shown catalytic activity in CO oxidation consistent with their oxygen storage capacity (OSC) values [110]. The deposition–precipitation method was used by Ta et al. [86] for depositing Au nanoparticles on CeO_{2-y}. The use of this method has been extended to other M/CeO_2 catalysts, especially Pt, Pd and Ni, by Cargnello et al. [111].

In a similar way, catalysts with transition metals deposited on CeO_{2-y} and $Zr_xCe_{1-x}O_{2-y}$ nanoparticles were also obtained, for example, a series of K, $Co/Zr_xCe_{1-x}O_{2-y}$ catalysts using the sol–gel method with subsequent deposition–precipitation of Co and K on the solid solutions $Zr_xCe_{1-x}O_{2-y}$ [112]. Increases in the OSC values, catalysts' sintering resistance and reducibility as well as activity in the oxidation of diesel soot with increased Zr contents were reported. The K promotion of $Co/Zr_xCe_{1-x}O_{2-y}$ resulted in the highest catalytic activity which the authors related to greater availability of active oxygen species, both adsorbed and networked. Alkali promotion (K and Cs) was frequently used to improve catalytic activity in redox reactions, for example, K in diesel soot combustion on $Ce_{0.65}Zr_{0.35}O_2$ monoliths [113] and Na in N_2O decomposition on CuO-CeO_2 mixed oxides [78].

In our laboratory, $Mn_xCe_{1-x}O_{2-y}$ and $Co_xCe_{1-x}O_{2-}$ nanoparticles were deposited on micrometric α-Al_2O_3 particles using the modified reverse nanoemulsion one-step technique, which enables direct preparation of nanocrystalline solid solutions and mixed oxides, as is described in the next paragraph [3,5,67]. These deposited nanoparticles consisting of solid-solution nanocrystals decorated and retained their specific catalytic activity on the inert α-alumina support.

The reverse microemulsion-mediated technique for formation of nanosized particles was proposed by Zarur and Jing [9]. Using this method, obtained nanosized particles should be much more homogeneous than those obtained by the other methods. Wang et al. [30] conducted a comprehensive structural study (synchrotron-based XRD, X-ray absorption and Raman spectroscopies and density functional calculations) to determine the possibility of incorporating Cu ions into the CeO_2 cubic network and to determine their location in this network. The Rietveld refinement of the high-Q X-ray diffraction data as well as density functional calculations indicated Cu substitution of Ce in the cubic ceria lattice coexisting with formation of O vacancies. This substitution caused strong structural distortions manifested by the pseudo-8 coordination number of Cu. Only four of the oxygen atoms remain in the immediate vicinity, and the other two are 0.04 and 0.11 nm away [30]. Such strong structural distortions certainly contribute to the increase in the lattice parameter of $Cu_xCe_{1-x}O_{2-y}$ with an increase in x despite the simultaneous increase in the concentration of O vacancies observed by Molenda et al. [11].

In our laboratory, we have developed a one-stage precipitation method for obtaining ceria-based $M_xCe_{1-x}O_{2-y}$ nanoparticles with several transition metals to check the formation of single-phase solid solutions (SPhSSs) by mixing two suitable inverted nanoemulsions (w/o) [11,12]. This method eliminates the stage of preparing the nanoparticles of ceria carriers in the first stage, on which precursors of metals or their oxides would be deposited, usually by the deposition–precipitation technique, in the second stage. Both nanoemulsions were prepared using cyclohexane as the oil phase and Triton X-100 as surfactant with n-hexanol as co-surfactant. Solutions of Ce and transition metal salts in appropriate ratios were nanoemulsions in the first and a water solution of the precipitating agents in the second. All the tested agents, namely TPAH (tetrapropylammonium hydroxide), TEAH (tetra ethylammonium hydroxide), NaOH, NH_3 and $(NH_4)_2CO_3$, proved to be effective, with a slight preference toward tetraalkylammonium hydroxides. The precipitation reactions took place in a large number of nanoreactors ($10 < d < 50$ nm), which were individual nanodrops of the water phase. After separation, drying and optimized thermal treatment, based on results of the thermal analysis coupled with mass spectra analysis of the evolved gas [12], nanocrystals ($2 < d < 4$ nm) forming highly porous aggregates ($10 < D < 20$ nm) were obtained.

The formation of nanocrystals of SPSSs was confirmed. The transition metal ions in the cubic CeO_2 structure were solved up to a limited x value ranging (depending on the applied M) from about 0.15 to 0.25 in the formula $M_xCe_{1-x}O_{2-y}$. Above these limits, a spontaneous separation or/and segregation of the MO_x phase took place. Our trials to obtain the inverted solid solutions failed, so the solid solutions of CeO_2 in Cu, Mn and Co oxide phases using the same modified method failed. From about 1 at% of CeO_2, the strongest line (111) of this oxide appeared among the dominated lines of CuO, Mn_3O_4 and Co_3O_4 [3,5,67].

In the case of CuO-CeO_2, single-phase solid solutions of Cu^{2+} in the cubic CeO_2 are formed as nanocrystals of $Cu_xCe_{1-x}O_{2-y}$ for $0.12 < x < 0.15$. At $x = 0.15$, the reflections at 2 Θ of 35.5° and 38.8° characteristic for the CuO phase were found in the XRD patterns [12,67]. The reference catalysts CuO-CeO_2 obtained by the wetness incipient impregnation method using the same starting solutions and commercial nanoparticles of CeO_2 provided biphase nanoparticles, although the same conditions of precipitation, maturation, drying and calcination were maintained. The CeO_2 pores were clogged by the CuO phase covering CeO_2 nanoparticles, causing a drastic reduction in the surface area and, thus, a drastic loss in the activity during total oxidation of methanol. The measured T_{100} values were equal to 225 and 370 °C, respectively [67].

The $Co_xCe_{1-x}O_{2-y}$ solid solutions obtained by the modified reverse nanoemulsion method were the only phase up to about x = 0.2, when separate Co_3O_4 crystallization began, resulting in an appearance of the most intensive diffraction line (311) of Co_3O_4 at $2\,\Theta = 37°$. References [3,114], reported the separation of Co_3O_4 in the course of $Co_xCe_{1-x}O_{2-y}$ preparation at the atomic ratio Co:Ce = 2:3, though the strongest (311) Co_3O_4 line was noticeable in their published XRD results at lower Co contents, even at Co:Ce = 1:4, as it was in our case [3]. Taking into account both of these results, one may assume that, in case of $Co_xCe_{1-x}O_{2-}$, the separation of the Co_3O_4 phase begins when, on average, in a crystallite containing five cubic unit cells of CeO_2, in four of those, one Ce atom is replaced with a Co atom, in other words, when, on average, 4 Ce atoms out of the 20 Ce atoms contained in the 5 CeO_2 unit cells are exchanged for Co. In case of Co-rich nanoparticle materials obtained by the same method, no solution of Ce in Co_3O_4 was present; only a nanocomposite of the CeO_{2-y} nanocrystals and twice-bigger Co_3O_4 nanocrystals were present in the range $0.85 < x < 1$.

Synthesis of the solid solutions of $Mn_xCe_{1-x}O_{2-y}$ using the one-step modified nanoemulsion method, described above, allows one to obtain nanoparticles composed of this SPSS up to about x = 0.25 [5]. Using the method of imaging, it can be assumed that the extraction of the spinel phase begins when, on average, in each unit cell of cubic $Mn_xCe_{1-x}O_{2-y}$ phase, there is one Mn atom instead of a Ce atom. For $Cu_xCe_{1-x}O_{2-y}$, separation of the CuO phase begins when, on average, in each unit CeO_2 cell, one half of a Ce atom is exchanged for Cu and, in the case of Co_xCeO_{2-y}, it shall happen if three-quarters of a Ce atom is exchanged for Co. Therefore, the highest solubility of the transition metal in CeO_2 phase, measured by the x_{max} values, clearly depends on the maximum valence, at least of these three metals in their oxides.

The size of the single-phase crystals of $Mn_xCe_{1-x}O_{2-y}$ was from 2 to 5 nm, increasing with x. After exceeding this limit value, the final product becomes two-phase; the Mn_3O_4 phase appears additionally. Synthesis of Mn-rich nanoparticles resulted in biphasic products confirmed by electron microscopy, and even at 1% Ce content, the most intense line (111) of CeO_2 appeared in XRD patterns. The Mn-rich product should be presented rather as Mn_3O_4-CeO_2 mixed oxides and not by the formula $Mn_xCe_{1-x}O_{2-y}$ suggesting formation of any solid-state solutions.

Hydrothermal and solvothermal syntheses are preferred for the production of larger amounts of nanometric material. Hydrothermal synthesis consists in long-term heating in a closed autoclave at temperature close to the boiling point of the water solution of metal salts with the addition of a precipitating agent. By appropriately manipulating the process parameters (concentrations, temperature, time), nanomaterials with specific shapes and catalytic properties (OSC, activity and selectivity) can be obtained. It is also possible to obtain the SPhSS of $Zr_xCe_{1-x}O_{2-y}$ starting from salt and NaOH solutions and an oxidizing agent (H_2O_2 or $NaBrO_3$) using the hydrothermal method [115]. Papadopoulous et al. [116] proposed a novel hydrothermal synthesis for Cu-promoted ceria catalysts using citric acid as a chelating agent and NaOH to obtain atomically dispersed Cu ions, which was confirmed by EPR analysis. These catalysts were characterized by a clearly increased catalytic activity.

Hydrothermal synthesis also allows one to obtain mesoporous materials. Xiao et al. [117], starting from an aqueous solution of metal salts, glucose and acrylamide and ammonia as a precipitating agent, obtained flower-like mesoporous materials $Ce_{0.9}M_{0.1}O_{2-y}$, where M = Y, La, Zr, Pr and Sn. The synthesis products were initially calcined at 600 °C in Ar and then at 400 °C in air. In order to obtain the highest catalytic activity in CO oxidation, they were activated by a reduction in the H_2/Ar stream at 800 °C.

Si et al. [118] obtained, using the hydrothermal method, homogeneous solid-state solutions of trivalent rare earths in $Ce_xZr_{1-x}O_2$ (x = 0.4–0.6). They reported that the larger ions of rare metals are more stable in the ceria-zirconia nanomaterial lattices. The effect of ammonia concentration during hydrothermal synthesis on the structure and redox properties of $Zr_xCe_{1-x}O_2$ solid solutions was determined by Zhang et al. [119]. Using non-equilibrium supercritical hydrothermal synthesis, Zhu et al. [120] obtained highly Cr-substituted CeO_{2-x} nanoparticles. These materials were characterized by sufficiently high oxygen storage capacity, which enabled the upgrading of bitumens at low temperatures.

An interesting modification of the hydrothermal method is its supplementation by the precipitation deposition. $Zr_xCe_{1-x}O_{2-y}$ nanotubes with a length of several hundred nm were obtained in such a way. A ZrO_2 nanosuspension in a water solution of cerium nitrate with NaOH as a precipitation agent was conditioned for hours in a closed autoclave [66]. These nanotubes were highly active in the conversion of ethanol to hydrogen, which the authors attribute to the dominant exposure of the most active crystal faces (100) and (110). $Zr_{0.5}Ce_{0.5}O_{2-y}$ nanoparticles with a size below 10 nm, obtained using the supercritical solvothermal method in polyethylene glycol, had an exceptionally high OSC value [121].

Sometimes, the method of deposited precipitation is supplemented by hydrothermal treatment of the product. This provided a zirconium cerium catalyst supported on SBA-15 for the oxidative dehydrogenation of ethylbenzene to styrene using CO_2 [122]. Due to the ordered mesoporous structure of SBA-15, this synthesis could also be qualified as co-precipitation using a solid template. Xi et al. [123] prepared bimetallic catalysts $Ni_xCo_{(10-x)}$/SBA-15 by co-precipitation deposition on a solid template using urea as a precipitation agent. The highest activity, coke and sintering resistance was determined for the 4–5 nm metal particles in the dry reforming of methane. Various structural and physicochemical analyses showed embedding of Ni and Co nanoparticles into the channel of SBA-15 with the formation of alloys. The highest activity, stability and H_2/CO molar ratio (close to 1) measured during 50 h of operation at a gas hourly space velocity of 72,000 mL/(g_{cat} h) under 973 and 1073 K, with no coke deposition, was found for the Ni_9Co_1/SBA-15 catalyst.

The greatest opportunities in controlling the synthesis of CeO_{2-y} and $M_xCe_{1-x}O_{2-y}$ nanomaterials are provided using appropriate molecular templates (soft templates) made of liquid crystals or surfactant molecules organizing into a specific template depending on the applied parameters of the solution state (T, c_i, pH). In this colloidal template, nanoparticles of precursors of oxide systems with shapes forced by the template are nucleated and grow. They are then subjected to washing, drying and thermal treatment in a controlled atmosphere leading to the transformation of the precursors into oxide systems and stabilizing their structure in future catalytic action. Examples of such nanostructured catalysts are $Cu_xCe_{1-x}O_{2-y}$ [124] and $Pt/Zr_{0.3}Y_{0.1}Ce_{0.6}O_{2-y}$ [125]. In the latter referenced work, Pt nanoparticles were embedded in a colloidal crystal template of yttrium-doped ceria-zirconia which in further processing turned into a macroporous catalyst $Pt/Zr_{0.3}Y_{0.1}Ce_{0.6}O_{2-y}$ highly effective in low-temperature methane combustion. Hollow nanospheres or nanotubes can be produced in this way [126–128]. Using appropriate templates, researchers were able to produce hollow nanospheres or nanotubes.

Solids or hard templates with a hierarchical porous structure, such as SBA-15, zeolites or polymers, characterized by large specific surfaces and porosity, are also used. In such a way, Rombi et al. [129] obtained highly active $Ni_xCe_{1-x}O_{2-y}$ catalysts for CO methanation. Furthermore, Li et al. [130], using a combination of two templates, namely the molecular triblock copolymer Pluronic F127 and solid-state polymethyl methacrylate micro-spheres, obtained nanocrystals of $Ce_{0.6}Zr_{0.4}O_{2-y}$ and $Ce_{0.7}Zr_{0.3}O_{2-y}$. These materials had a three-dimensional ordered macroporous structure with hollow mesoporous (warm-like) channels in the walls. The sizes of these nanocrystals were in the range of 4–7 nm. Rood et al. [131] used graphene oxide as a solid template to obtain enhanced ceria nanoflakes effective in CO oxidation and dry reforming of methane.

The use of templates requires their removal after synthesis, which is often not a trivial task. For this reason, methods that do not require the use of surfactants and templates are still used [17,68]. This is because by maneuvering only the parameters of hydrothermal and solvothermal processes, it is possible to obtain ceria-based nanoparticles of various shapes, for example, nanotubes [132–134] or hollow nanocubes, using peracetic acid as an oxidant and without templates [135].

During the synthesis of nanometric systems, there are always stages of precursor heating and calcination, which, especially in mass synthesis, are associated with temperature and concentration gradients of reagents. Reducing the impact of these factors on the heterogeneity of the obtained products can be achieved, especially in aqueous and alcoholic environments, by microwave heating, which additionally shortens the operation time and reduces the likelihood of contamination of the product by heaters and furnace walls. These issues were the subject of a monograph published by Reddy's group with an emphasis on automotive catalytic converters [136]. The use of microwave heating allowed researchers to obtain a higher concentration of zirconium in the cubic fluorite-type $Zr_{0.4}Ce_{0.6}O_{2-y}$ solid-solution phase [137]. In this solution, a much greater share of oxygen atoms shifted to tetragonal positions, manifested in the Raman spectrum, were associated with exceptionally high catalytic activity in CO oxidation compared to catalysts heated in classic furnaces. Similar benefits are provided by the use of ultrasonic treatment in the synthesis of nanomaterial precursors, which was generally presented by Bang and Suslick [138]. In this way, Alammar et al. [139], starting from ionic liquids, obtained nanoparticles of CeO_{2-y} characterized by increased activity in CO oxidation.

The often encountered thermal activated restructuring of the CeO_2 surface also plays an important role. Tinoco et al. reported that annealing, in oxidizing conditions (873 K), of the exposed (100) walls leads to their restructuring into a zig-zag series of (111) facets [140]. The Au nanoparticles (2–3 nm) were preferentially located in the valleys between these (111) zig-zag walls on the periphery of the CeO_2 nanoparticles with a previously restructured surface. Cargnello et al. [111] applied this procedure to other metals as well, including Pt, Pd and Ni. Also, the operating conditions of the catalyst may contribute to a significant reorganization of the bimetallic particles deposited on the cerium support. This was observed by Soler et al. [89] during steam reforming of ethanol into Rh and Pd/CeO_2.

Combustion is often used for synthesis of nanomaterials as a fast method and shortens the sequence of synthesis processes, although it allows one to obtain materials with a not especially high surface area. It uses an oxidant, e.g., in the form of metal nitrates, and a reducer, usually organic fuel. Heating this mixture ignites the system and produces nanoparticles and exhaust gases. Sometimes, this simple combustion method results in high-surface-area materials. For example, Chen et al. [141] obtained mesoporous ceria-zirconia solid solutions with a specific surface area of 90–208 m^2/g using a modified combustion method. The authors used salt-assisted combustion with ethylene glycol as fuel. The urea nitrate combustion method for the preparation of $CuO/CeO_2/ZrO_2/Al_2O_3$ catalysts was compared by Baneshi et al. [142] with the same composed catalysts obtained using a homogeneous co-precipitation method. The second method provided smaller Cu crystallites and better surface dispersion. In consequence, the catalytic activity in methanol steam reforming was higher, though the first catalysts produced less CO—which is more convenient for applying such produced hydrogen in fuel cells.

Great hopes are associated with flame spray pyrolysis, which allows for direct one-step procurement of nanoparticles. This method reduces the impact on the environment, shortens the time and lowers the price of catalyst production on a larger scale. Kim and Laine [143] obtained nanometric catalysts $(Ce_{0.7}Zr_{0.3}O_2)_x(Al_2O_3)_{1-x}[(Ce_{0.7}Zr_{0.3}O_2)@Al_2O_3]$ of the core–shell type using organometallic precursors dissolved in ethanol and, after being converted into an oxygen aerosol, these catalysts were blown into a flame of combusted methane at a temperature above 1500 °C. The aerosol stream was then quenched at a rate of 1000 °C/s, and the product nanoparticles underwent electrostatic precipitation in an unaggregated form with a size not exceeding 20 nm. Strobel and Pratsinis [144] investigated the influence of the chemical composition of the precursor solvent on the morphology, structure and properties of the obtained nanoparticles. Sun et al. [145] described the use of several metal–organic frameworks (Ce-MOFs) synthesized by pyrolysis in toluene incineration as a representative of VOCs. The authors showed that the catalytic performance of catalysts with the smallest particles, the largest specific surface area, the highest concentration of surface oxygen species and the easiest reproducibility is best. These statements are, as it were, a summary of the general knowledge about the activity of oxidation reaction catalysts. Woźniak et al. [8] synthesized, by oxidative thermolysis of $Ce_{0.9}REE_{0.1}(HCOO)_3$ mixed formate, star-like $Ce_{0.9}REE_{0.1}O_{1.95}$ mixed oxides. These hierarchically structured star-shaped particles were compared with microemulsion-derived, loosely arranged nanoparticles. The proposed catalysts had higher activity in the soot combustion process.

Mechanochemical synthesis is often used to obtain nanomaterials, especially in the large-scale production of ceria-based catalysts. It consists in long-term intensive grinding in mills (reactive milling) of macro-grain mixtures of starting chemical compounds. This grinding leads to fragmentation, accumulation of energy, creation of defects and chemical reaction with formation of new reactive nanomaterials, e.g., mixed oxides. The general principles and application of this technique have been described in many review articles such as [146–149].

Mechanochemical synthesis is generally carried out at ambient temperature, which reduces energy consumption, and without organic solvents. Therefore, it is a green technology that complies with the principles of sustainable development of chemical technology. Considering this need, IUPAC included mechanochemistry as one of the 10 most important innovative technologies implementing this goal in the 21st century [150]. Moreover, due to the simplicity of the processing parameters, the adaptation of mechanochemical synthesis from lab benchtops to commercial-scale production took less than 8 years [150]. In order to facilitate the transfer of laboratory test results to an industrial scale, an attempt was made to standardize synthesis reports on a laboratory scale [151].

It is likely that Trovalleri et al. [152] were the first to use ball milling for the synthesis of mixed nanosized ceria-zirconia nanoparticles $Ce_{0.5}Zr_{0.5}O_{2-y}$. They found that prolonging the milling beyond 9 h did not result in any further improvement in the product's reducibility, which is related to the OSC and redox activity of the ceria-based catalysts. Frequently, steel ball mills contaminate the obtained nanoparticles with Fe and W. To avoid this, Cutrufello et al. [153] used a ceramic zirconium ball mill to obtain uncontaminated ceria-zirconia nanocatalysts for dehydrogenation of 4-methylpentan-2-ol. A review on the mechanochemical synthesis of ZrO_2 nanoparticles was presented by Dodd and McCormick [154].

Often, a liquid component is added to the mill. For example, Zheng et al. [155], starting from $ZrOCl_2 \cdot 2H_2O$, $Ce_2(CO_3)_3$ and $H_2C_2O_4 \cdot 2H_2O$, added various surfactants to ground substrates. The largest specific surface areas (>80 m^2/g) of $Zr_xCe_{1-x}O_{2-y}$ nanoparticles were obtained using neutral surfactants and these carriers were the best for the subsequent deposition–precipitation of Pd and Rh in the production of TWC car catalysts. Tsuzuki and McCormick [156] showed that the addition of a significant excess of NaCl as a diluent to the stoichiometric mixture of $CeCl_3$ and NaOH eliminated the often occurring ignition of the ground reagents during milling, which occurs even in Ar, resulting in the formation of large (500 nm) aggregates of CeO_{2-y}. Li et al. [157] added higher amounts of NaCl and eliminated ignition, obtaining nanoparticles of size 40–70 nm. Starting from $(NH_4)_2Ce(NO_3)_6$ instead of $CeCl_3$ and also using NaCl as an inhibitor of agglomeration, Li et al. [158] obtained ceria nanoparticles as small as 2.5 nm. The way NaCl acts to obtain highly active nanoparticles of CeO_2 was discussed by Shu et al. [159] [Shu, Y. et al., 2020]. Cheng, H., et al. [160] presented a low-cost and solvent-free large-scale mechanochemical nanocasting method for obtaining highly porous $CeMnO_x$ catalysts for low-temperature NH_3-SCR of NO_x. These catalysts show high specific area and their reach in chemisorbed species allows for 100% conversion of NO_x at 150 °C.

An innovative method of obtaining CeO_2-based catalysts has recently been presented by the Llorca group [161]. They obtained ceria aggregates such as woodpile with micrometric channels from ceria powder paste with nitric acid using a 3D printer. The materials obtained in this way, after applying Ni on them, were tested in the ammonia decomposition reaction. They turned out to be more active under the same reactor conditions than the conventional catalysts of cordierite honeycomb wash-coated with Ni/CeO_2.

Although this review focuses on the methods of preparing ceria-based catalysts, selected examples of individual syntheses also include the results of using the obtained catalysts in specific reactions. Most often it was CO oxidation, because it is the most common test of general redox activity, next to TPR and TPO. Information on the reactions tested in the cited publications is summarized in Table 1.

Table 1. Examples of ceria-based catalysts applied for various chemical processes.

Reaction	Catalyst	Ref.
CO oxidation	• RuO_2/CeO_2 with ultra-large mesopores	[1]
	• Au nanoparticles supported over nanoshaped CeO_2	[33]
	• CuO/CeO_2—different shaped nanocatalysts	[68]
	• CuO-CeO_2-ZrO_2—flower-like morphology	[70]
	• Au nanoparticles on {100}, {111} and {111} nanofacetted structures of CeO_2	[94]
	• CeO_2 catalysts	[85]
	• Thermally reconstructed CeO_2 nanocubes	[87]
	• CeO_2 nanocatalyst	[95]
	• Nanostructured $Co_xCe_{1-x}O_y$	[114]
	• Cu-promoted CeO_2 catalysts	[116]
	• Doped CeO_2—mesoporous flower-like morphology	[117]
	• CeO_2 nanoplates, nanotubes and nanorods	[127]
	• CeO_2 nanoflakes—graphene oxide as template	[131]
	• Nanostructured $Ce_xZr_{1-x}O_2$	[137]
	• Sonochemically prepared CeO_2 nanoparticles	[139]
Diesel soot oxidation	• CeO_2-ZrO_2 nanocubes	[91]
	• CoO_x-decorated CeO_2 heterostructures	[108]
	• CeO_2/ZrO_2 prepared by sol–gel method	[112]
	• K-promoted $Ce_{0.65}Zr_{0.35}O_2$ monolithic catalysts	[113]
Ethanol steam reforming	• Rh-Pd/CeO_2 nanocubes and nanorods	[89]
	• Ir/CeO_2 nanocatalysts	[93]
	• Nanostructured $CuO/CeO_2/ZrO_2/Al_2O_3$	[142]
Dry reforming of methane	• MOF-derived Ni/CeO_2 catalyst	[21]
	• CeO_2 nanoflakes—graphene oxide as sacrificial template	[131]
Low-temperature methanol combustion	• $Co_xCe_{1-x}O_y$ nanocatalysts	[3]
	• Nanocomposite catalysts $Mn_xCe_{1-x}O_2/\gamma$-Al_2O_3	[5]
	• Nanometric Ce_{1-x} $Cu_xO_{(2-\delta)}$ materials	[12,24,67]
	• Nanowire hierarchical CeO_2 micro-spheres	[6]
	• Catalysts prepared by Ce-MOFs pyrolysis	[145]
Methane combustion	• Macroporous $Ce_{0.6}Zr_{0.3}Y_{0.1}O_2$	[125]
Combustion of polycyclic aromatic hydrocarbons	• Nanostructured CeO_2	[16]
Fast pyrolysis of organic vapors	• Hierarchically structured CeO_2	[7]
HCl oxidation with O_2 to obtain Cl_2	• Mesoporous CeO_2	[15]
NO reduction with CO	• Oxidized and reduced NiO_x/CeO_2	[50]
NH_3-SCR	• Highly porous $CeMnO_x$	[160]
NH_3 decomposition	• 3D-printed CeO_2 structures loaded with Ni	[161]
Carboxylative coupling using CO_2	• Mesoporous CeO_2-supported Ag	[2]
Dehydrogenation of ethylbenzene to styrene with CO_2	• CeO_2-ZrO_2/SBA-15	[122]
4-methylpentan-2-ol dehydration	• Nanophase CeO_2-ZrO_2 nanocubes	[153]
Oxidation of benzyl alcohol with TBHP	• Mesoporous CeO_2	[4]
Oxidation of benzyl alcohol with O_2	• Au-CeO_2 catalysts	[100]
Low-temperature bitumen upgrading	• Cr-substituted CeO_2 nanoparticles	[120]

4. Conclusions and Outlook

Non-stoichiometric CeO_{2-y} nanocrystals and their aggregates seem to be necessary ingredients of redox catalysts' operation according to the Mars–Van Krevelen mechanism. This is due to the high reversible OSC values obtained by maintaining the essential crystal structure during redox cycles. This makes it possible to act as an oxygen buffer during catalytic reactions. In addition, active oxygen species (O_2^{n-}, O^-) are generated on active oxygen vacancy–Ce^{3+} complexes. This is particularly important in low-temperature processes of complete oxidation of volatile organic compounds, protection against loss of catalyst activity as a result of deposition of carbon deposits blocking active sites and regeneration of catalysts. Due to its thermal stability, CeO_2, and especially its $Zr_xCe_{1-x}O_2$ solid-state solutions and mixed oxides CeO_2-ZrO_2, can act as a stable catalytic carrier and activity improver of the transition metal or its oxide. The crystal lattices of both of these oxides are relatively flexible, able to accept transition metal ions, ensuring their high dispersion and protecting them against sintering. It can be assumed that their use as active ingredients in many different new catalytic processes will spread in the future.

This review presents all the methods used to obtain ceria-based nanocrystalline catalytic systems, both one- and two-stage, starting from simple methods of precipitation and co-precipitation and ending with a 3D printing method. The methods of deposition of nanoparticles of active noble metals and transition metal oxides as well as the creation of solid-state solutions of transition metals in ceria lattices are also discussed. All these methods of catalyst synthesis are supported by representative examples of their application in specific reactions. We believe that this review will be helpful for the reader who wants to quickly get an overview of all the methods used for the synthesis of ceria-based nanocatalysts and to choose the right method for the development of a catalyst for a chosen reaction.

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