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Review

Structure, synthesis, and catalytic properties of nanosize cerium-zirconium-based solid solutions in environmental catalysis

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ABSTRACT

Nanosize cerium-zirconium solid solution (CZO) with a special fluorite structure has received an increasing research interest due to their remarkable advantages such as excellent oxygen storage capacity and great flexibility in their composition and structure. By partial metal (including rare earth, transition, alkaline earth or other metal) doping into CZO, the physicochemical properties of these catalytic materials can be controllably adjusted for the study of specific reactions. To date, nanosize CZO has been prepared by co-precipitation, sol-gel, surfactant-assisted approach, solution combustion, micro-emulsion, high energy mechanical milling, etc. The advent of these methodologies has prompted researchers to construct well-defined networks with customized micromorphology and functionalities. In this review, we describe not only the basic structure and synthetic strategies of CZO, but also their relevant applications in environmental catalysis, such as the purification for CO, nitrogen oxides (NO_x), volatile organic compounds (VOC), soot, hydrocarbon (HC), CO₂ and solid particulate matters (PM), and some reaction mechanisms are also summarized.

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1. Introduction

Nowadays, the issue of the environment is receiving ever increasing attention. One of the primary efforts of environmental protection is concentrated on controlling the emission of toxic pollutants from combustion of fossil fuels in automotive engines and industrial production [1–3]. Three-way catalysts (TWCs) are widely employed to lessen the emissions of carbon monoxide (CO), nitrogen oxides (NO_x), and hydrocarbons (HC) from automobile exhausts [4–6]. Among these catalysts, ceria (CeO₂) is a key component, which exhibits cubic fluorite type of structure and has attracted much attention in recent decades due to its good redox property and high storage/release oxygen capacity, associated with the abundant oxygen vacancy and facile shift of Ce³⁺/Ce⁴⁺ [7–10]. It has also been used in many

heterogeneous catalytic reactions [11–18], including methane combustion, water-gas shift, water steam reforming reaction, etc. Moreover, a large number of reports have shown that partial incorporation of zirconium ion (Zr⁴⁺) into ceria lattice can substantially enhance the redox properties and oxygen storage capacity (OSC) [19–30]. This is an interesting finding, considered that Zr⁴⁺ is isovalent with the host Ce⁴⁺ ion and also a fixed valent ion, so that it can not induce the valency change such as with Pr^{3+/4+} or creation of charge compensating defects such as with Gd³⁺ [31–35]. Instead, the smaller Zr⁴⁺, in comparison with Ce⁴⁺, prefers a 7-fold coordination, in contrast to the 8-fold coordination of the fluorite cation, resulting in a driving force to form oxygen vacancies associated with structural relaxation through reduction of the smaller Ce⁴⁺ to the bigger Ce³⁺ [36–39]. Based on the first principle calculations, a Zr dopant

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acts as low energy regions for the formation and clustering of oxygen vacancy [40–43]. In addition, the long-term thermal morphology and/or redox stability of pure CeO_2 has been enhanced by the introduction of Zr [20,28,44,45]. Furthermore, owing to the special redox ability of Ce-Zr solid solution (CZO), it can be employed to support noble metals and transition metal oxides or to design ternary solid solutions by doping small amounts of other transition or rare earth metals [46–53]. CZO has been widely employed in the abatement of CO , NO_x and toxic volatile organic compounds (VOC) and many other heterogeneous catalysis reactions. This review primarily focuses on the structure, synthesis, and application of Ce-Zr-based solid solutions in environmental catalysis. The first part of the review presents advances in the structure and synthesis of CZO, and the catalytic properties of CZO are thereafter reviewed in the second part.

2. The structure of nanosize cerium-zirconium-based solid solutions

Ceria has a special cubic fluorite structure and is the most widely used rare earth oxide. It is also a good catalyst support that can promote the uniform distribution of active components and enhance the catalytic activity [17]. However, pure ceria easily aggregates at high temperatures, and Zr doping can enhance the stability of cerium-based materials. CZO exhibits a main cubic fluorite structure when Zr content is low, as shown in Fig. 1. However, CZO undergoes a cubic to tetragonal fluorite phase transition with increasing Zr content and ultimately forms a monoclinic phase at high Zr contents [39,54–56]. The bond length ratio of c - to a -axis (c/a) is equal to 1.4 for the tetragonal phase (t -phase), which is attributed to the $P4_2/nmc$ space group and shows two distortions t' ($c/a = 1.01$) and t'' ($c/a = 1$) [57]. One can distinguish between the t' and t'' phases from the measurement of lattice parameters, though some similarity between the t'' and cubic structures. The phase change from cubic to t'' would induce an increase in the wavenumber of Raman vibrational modes and remarkable changes in ionic bond strength [54,58]. Similar to the cubic to tetragonal distortion in CZO, the relaxation of oxygen atoms away from their ideal fluorite positions and the formation of ordered domains have been observed in cubic fluorite and hafnia by electron diffraction. The structure of CZO materials exhibits some primary features, which have been reported by Yashima and Fábregas *et al.* [59,60]. One of the important features is that the

Fig. 1. Schematic diagram of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ lattice structure: ● O, ● Zr, and ● Ce.

first oxygen shell around Ce exhibits the characteristics expected for pure CeO_2 (fluorite-type crystal structure, one shell with 8 oxygen atoms) even if the crystallite phase is t' (t' and t'' forms) or c . In contrast, the first shell around Zr atoms shows obvious differences from the changes in the crystal structure. This means that it splits into two oxygen subshells for the tetragonal forms and displays only one shell for the c phase. In other words, the tetragonal-to-cubic phase transition is closely related to a symmetry change of the first oxygen shell around Zr atoms, whereas that around Ce atoms remains unchanged. The appearance of cubic, t' , and t'' phases in CZO depends strongly on the Zr content. Yashima *et al.* [54] proposed a phase diagram according to XRD and Raman analysis, as shown in Fig. 2, and it could be depicted as follows. A cubic fluorite phase c is present (group $Fm3m$) for $x > 0.85$ at temperature below 1000 °C. A tetragonal phase t (group $P4_2/nmc$) can be produced at high temperature by solid-state synthesis and then cooling to room temperature for $0.10 < x < 0.30$, and it is thermodynamical stable. A monoclinic phase (group $P2_1/c$) is formed for $x < 0.10$, while a metastable phase t' is seen for $0.30 < x < 0.65$. In the end, t'' or pseudo-cubic phase is intermediate between the c and t' phases ($0.65 < x < 0.85$ or $0.5 < x < 0.85$ for small particles). This is characterized by a cubic cation sublattice, while its oxygen sublattice is tetragonally distorted ($P4_2/nmc$). The phase boundaries should be very approximate. As a matter of fact, in the case of the metastable tetragonal phases, the structure distortion of CZO should be highly depended on the calcination temperature and the particle size of the materials.

Due to the complexity of the phase diagram, it is difficult to determine the phase homogeneity of CZO, even though a great effort has been made. Small changes in oxygen ion-cation coor-

Fig. 2. Metastable-stable phase diagram in $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ tem: ● phase, □'-phase, ○'-phase, △'-phase. The dash lines represent the metastable phase boundaries. Reprinted from [54] with permission.

dination are not always detectable as additional peaks (or peak splitting) by XRD. However, Raman and other vibrational spectroscopy methods may be used to distinguish the primary oxygen ion distortions between the t'' and cubic phases [54]. Raman spectroscopy can play a critical role in the determination of all these phases and in the identification of the mechanical stress. In fact, laser-excited Raman spectra are extremely sensitive to M–O bonds, while powder XRD patterns are essentially determined by the arrangement of the lattice cations. Unfortunately, these conventional techniques fail in the investigation of the low crystallization degree materials, however, which are very important in heterogeneous catalysis. More advanced techniques, such as neutron diffraction and EXAFS, have proved to be effectively on determining inhomogeneity and detecting complementary structural information [36,62–65]. Moreover, Montini *et al.* [66] investigated the potential of luminescence spectroscopy for identifying the homogeneity of CZO materials using Eu(III) ion as a structural probe. This technique provides a detailed picture of local environment of the cations in these materials due to the fact that the luminescence properties of Eu(III) are strongly affected by the local surrounding around the cation ion (Fig. 3).

Great efforts to establish a correlation between structure and physicochemical properties have been devoted to a lot of research concerning CZO materials. The presence of surface domains [67,68], formation of ordered defective structures [69–71], disordered oxygens coordinated around zirconium [72], and distortion in the oxygen sublattice [38,66–68] have improved redox properties of CZO with respect to CeO_2 . Com-

parison of CZO powders with different particle sizes between ~6 and 80 nm, the phase boundaries exhibit an apparent shift to slightly higher zirconia contents with the decrease of the particle size and the increase of the solubility of zirconia in each phase [73]. The position of the phase boundaries for CZO can only be taken as approximate because t' and t'' are metastable phases and the degree of distortion of the cubic fluorite structure strongly depends on the synthesis method, particle size, morphology, metal doping and supported active phase type [74].

3. Recent advances in the synthesis and morphology of nanosize cerium-zirconium-based solid solutions

It is well known that morphology and microstructure significantly influence the physicochemical properties and the performances of CZO materials, especially the high surface area, which can supply a large number of active sites for the proceeding of catalytic reactions [75]. Materials with nanosize (1–100 nm) will exhibit special properties due to the following effects: a) quantum size effect; b) small size effect; c) surface effect; d) macroscopic quantum tunneling effect. Hence, it is well worthy to pay attention and spare efforts on the study of the synthesis of nanosize CZO with different morphology and catalytic performances.

3.1. Synthesis methods for nanosize cerium-zirconium-based solid solutions

A synthesis method is significantly important for nanosize CZO due to its influence on the size, morphology, structure, surface state, and oxygen vacancies. It is closely related to the reducibility of cerium-based composite of the as-prepared materials [76–80]. The controllable synthesis research is an issue worthy to concern. To date, various synthetic routes have been developed for the synthesis of nanosize cerium-zirconium-based solid solutions, such as co-precipitation (CP), sol-gel (SG), self-assembly, template-assisted approach, solution combustion (SC), micro-emulsion (ME), high energy mechanical milling, etc.

3.1.1. Co-precipitation method

CP is one of the most commonly used methods for nanosize CZO synthesis owing to its simple synthesis process. In general, it includes room-temperature [81–85], medium-to-high temperature [86–88], surfactant-modified [89,90], and ultrasound-induced CP [91]. Precipitants (ammonia water and ammonium carbonate) are employed to react with the soluble components of cerium and zirconium compounds and form precipitate in soluble precursors. After a series of process of separation, washing, drying and calcination, the final products are obtained. The reaction is as follows (Eqs. (1)–(4)):

Fig. 3. Eu(III) emission spectra of the thermodynamically stable cubic Ce-Zr-EuO₂ (CZE) samples with the schematic representation of Eu surface site located on the stable (111) surface of cubic Ce_{0.8}Zr_{0.2}O₂ and of the single Eu bulk site in Ce_{0.8}Zr_{0.2}O₂ by EXAFS data. The details of ⁵D→⁷F₀ transition are reported for both surface and bulk Eu(III)-doped materials after different thermal treatments. (a) Surface-doped CZE calcination at 500 °C for 5 h; (b) Surface-doped CZE calcination at 1000 °C for 5 h; (c) Bulk-doped CZE calcination at 500 °C for 5 h; (d) Bulk-doped CZE calcination at 1000 °C for 5 h. Reprinted from [66] with permission.

This method can make an excellent mixing of the different components. The surface area of CZO prepared by this traditional CP method is 20–120 m²/g, which would decrease to about 20 m²/g after being calcined at 1000 °C. Hsiang *et al.* [92] prepared Ce_{0.6}Zr_{0.4}O₂ powders by the CP method and studied the correlation between the crystallite structure and reductive property. The results indicated that Ce_{0.6}Zr_{0.4}O₂ decomposed into Ce-rich (cubic) and Zr-rich (tetragonal) phases from a single cubic phase after being calcined above 1100 °C. Moreover, the cation diffusion may result in the structural alteration under reduction/re-oxidation treatment. In this synthesis process, because the precursors are made of hydroxides or salts of cerium and zirconium, a calcination process at high temperature is needed to form solid solution. Nevertheless, high temperature would lead to the loss of surface area seriously. Furthermore, during the drying process, the particles might aggregate due to the effect of surface tension of water (or other solvents). Therefore, a lot of improved ways were developed to enhance the property of nanosize CZO. Chen *et al.* [93] proposed a modified CP method with triethylamine assisting to prepare CZO with a big surface area and high thermal stability. They found that the adsorbed surfactant (triethylamine) on the surface of particles might form a protective layer, which could serve as an effective barrier to inhibit the grains from aggregating. Consequently, the added surfactants could remarkably improve the particle dispersion and increase the surface area of CZO.

3.1.2. Sol-gel method

The SG method is also widely used for nanosize CZO synthesis. Metal compounds are mixed with the highly active coordination compounds and undergo hydrolysis and condensation reaction to form sol and then transform to gel with three dimension net-work structure. Final products are obtained after drying and calcination. Generally, SG synthesis is a suitable method to prepare CZO with high degree of homogeneity by controlling hydrolysis of alkoxide or similar precursors. However, when the rates of hydrolysis between the two metals are quite different, it may be difficult to simultaneously hydrolyze both precursors, particularly when Zr(*n*-C₃H₇OH)₄ is employed as a precursor. Therefore, appropriate chemical modifications of the hydrolyzing process are needed to control the rate of hydrolysis. Meeyoo *et al.* [94] adopted an SG technique to prepare Ce_{1-x}Zr_xO₂ (*x* = 0~1.0) mixed oxide catalysts for CO oxidation. The initial solution was synthesized by mixing 0.4 mol/L of urea solution with 0.1 mol/L of metal salt solutions with volumetric ratio equal to 0.5, and the ratio was changed depending on the desired solid solution. The catalytic activities of these mixed oxide catalysts were found to be dependent on Ce/Zr ratio, and Ce_{0.75}Zr_{0.25}O₂ exhibited the highest CO conversion. Kozlov *et al.* [76] prepared an Al₂O₃-supported Ce_{0.45}Zr_{0.55}O₂ catalyst by a modified SG method. In this preparation process, 2-methyl-2,4-pentanediol was added to affect the substitution of the isopropoxy ligand by the diol. As a result, CZO exhibited a high content of readily reducible Ce⁴⁺. Additionally, the mixed oxide particles still retained small and homogeneous single phase even after reduction at 980 °C and reoxidation at 900 °C. Yu *et al.* [95] synthesized a series of

M-Ce_{0.7}Zr_{0.3}O₂ (M = Li, Na, K) using a modified SG method. In the synthesis process, a proper amount of citric acid (CA) was added to control the hydrolysis of precursors and then calcined at 600 °C for 6 h to obtain the final products. The as-prepared materials exhibited a higher catalytic activity for soot combustion than that prepared by the CP method.

3.1.3. Template-assisted method

The template-assisted method is widely employed for the preparation of nanostructural CZO due to the advantages of convenience, simplicity and inducing effect of various templates with special structures or morphology. Two types of templates are available as follows.

(a) Soft template

Surfactants can form micelles with different shape or morphology when dissolved into water up to a certain concentration, and thus the micelles can be used as templates for nanomaterial synthesis. In recent years, numerous studies have been reported on the use of cationic, anionic and nonionic surfactants as template to synthesize nanosize CZO with mesoporous structure [96]. The commonly used surfactants are cetyltrimethylammonium bromide (CTAB) and tri-block copolymers Pluronic P123 and F127. Trovarelli *et al.* [89] prepared CZO with high surface area by a soft template-assisted approach. In a typical preparation process, the mixed oxide was synthesized by adding an aqueous solution of the cationic surfactant CTAB to precursor solution made of hydroxides or salts of cerium and zirconium. Cationic surfactants effectively incorporated into cerium and zirconium hydrous oxides under basic conditions. The presence of cerium inhibited alkyl-trimethyl-ammonium salt acting as the template to form regular pore structure. The removal of surfactants after calcination gave rise to the formation of fluorite-structured CZO with high specific surface area. Yuan *et al.* [97] demonstrated a novel straightforward and reproducible method to prepare a highly ordered mesoporous CZO with a 2-D hexagonal structure. The general synthesis strategy was based on an SG method combined with evaporation-induced self-assembly (EISA) in ethanol, and P123 was used as the template and ceric nitrate and zirconium oxide chloride as the precursors. A series of mesoporous CZO with different Ce/Zr ratios was obtained under the optimal temperature and humidity conditions.

(b) Hard template

The ordinary hard templates contain porous anodic alumina (AAO), molecular sieves, carbon nanotubes (CNTs) and silica nanowires. They can be used as rigid templates for nanomaterial synthesis. Zamani *et al.* [98] prepared mesoporous CZO using mesoporous silica (SBA-15 and KIT-6) as template agents, which were impregnated with precursor materials. Structural analysis of the products confirmed the formation of mesostructures, and thermogravimetry measurements showed the remarkable increase of material OSC compared with pure ceria. In the case of Ce_{0.95}Zr_{0.05}O₂, response measurements showed the relatively fast and stable response of the sensor to oxygen-containing atmospheres.

Some special structures require specific hard templates. The three-dimensional ordered macroporous (3DOM) structure is

prepared via organic polymer templates such as polystyrene (PS), polymethyl methacrylate (PMMA), and polystyrene-methyl methacrylate-acrylic acid microspheres. Some works have been reported on this aspect [99–104]. Zhao *et al.* [102] prepared a series of 3DOM CZO using PMMA colloidal crystal as template agent, as shown in Fig. 4a. In a typical synthesis process, the first step was to prepare an ordered colloidal crystal template (CCT) with monodispersed PMMA spheres (444 nm) and PS spheres (454 nm). The second step was to synthesize the liquid precursor. The stoichiometric amount of cerium nitrate and zirconium oxide chloride were dissolved in an mixed solvent including ethylene glycol (EG) and methanol (20–40 vol%) followed by pouring into a volumetric flask. Then, the dried PMMA or PS colloidal crystal was soaked in the solution for several hours. Excess solution was removed by filtration. Finally, 3DOM CZO was obtained by removing the template via calcining at 650 °C for 5 h. The as-prepared $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ material exhibited a well-ordered 3DOM structure, which consisted of interconnected networks of spherical voids through open windows, ca. 120 nm in diameter, as shown in Fig. 4b and 4c. The walls of the macroporous samples were crystallized.

3.1.4. Hydrothermal and solvothermal method

The hydrothermal method refers to a synthesis route via reaction of species in the water media (solvent) under the condition of certain temperature (100–1000 °C) and pressure (1–100 MPa). It is well known that CP and SG methods can be used to prepare catalytic materials of high purity. However, the as-prepared materials usually show amorphous structures. Hydrothermal synthesis can overcome this drawback and may be regarded as an effective strategy for synthesis of specific nanosize catalytic materials in liquid phase. This technique has attracted more attention since the 1980s when nanocerium was first synthesized via a hydrothermal method by Matijevic *et al.* [105]. In the solvothermal method, organic solvents are employed instead of water. The whole process of hydrothermal or solvothermal synthesis is controllable and can be regarded as a

green chemistry process due to the very good control of volatilizing of organic solvents, non-toxic gas releasing. And the synthesis can conveniently obtain the nanomaterials with regular shape, size and crystallite phases. Walton *et al.* [106] reported a simple one-step hydrothermal method for preparation of nanocrystallite CZO, whose redox properties depended crucially on the reaction conditions. Ihm *et al.* [107] fabricated CZO by a continuous hydrothermal method in supercritical water. The supercritical synthesis led to CZO with better thermal stability and higher OSC than that synthesized by the CP method.

The solvothermal method is a direct and rapid method, which has been used for the synthesis of metal oxide nanoparticles (NPs) for various applications [108,109]. Devaraju *et al.* [110] adopted the solvothermal method under supercritical and high autogenous pressure conditions (400 °C, 40 MPa) for the direct preparation of nanocrystallite powders CZO, which exhibited a high OSC value.

3.1.5. Solution combustion method

The SC method is simple and fast, and yields high surface area products with desired composition. It is an attractive synthetic route especially for the preparation of multicomponent oxide materials because the homogeneity of the aqueous solution of the salts is preserved in the combustion residue. The materials prepared by this method not only possess better homogeneity and purity, but also have high surface areas. Reddy *et al.* [111] reported a single synthesis step of nanosize $\text{CeO}_2\text{-M}_x\text{O}_y$ mixed oxides ($\text{M}_x\text{O}_y = \text{SiO}_2, \text{TiO}_2, \text{ZrO}_2$ and Al_2O_3) by the SC method. Among these samples, $\text{CeO}_2\text{-SiO}_2$ showed the highest surface area compared with other oxides. The decreasing order of specific surface areas was as follows: $\text{CeO}_2\text{-SiO}_2$ (125 m^2/g) > $\text{CeO}_2\text{-TiO}_2$ (79 m^2/g) > $\text{CeO}_2\text{-ZrO}_2$ (56 m^2/g) > $\text{CeO}_2\text{-Al}_2\text{O}_3$ (38 m^2/g). Chen *et al.* [112] prepared mesoporous CZO via a salt-assisted combustion method using EG as the fuel and nitrate as the oxidant, and the effect of added salt on the properties of the products was studied. The presence of salt led to a more than 10-fold increase in the specific surface area of the products at a given molar ratio of EG/nitrate. It was owing to that the instant salt in-situ precipitation inhibited the formation of hard agglomerates and sintering of nanocrystallites. Therefore, this method provided a novel and effective strategy to tailor the material properties. Zhang *et al.* [113] synthesized $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ solid solutions by CP, SG, SC and template-assisted approaches. The catalytic activities of bulk and $\gamma\text{-Al}_2\text{O}_3$ supported $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ solid solutions were investigated for the oxidation of soluble organic fractions from diesel engine exhausts. $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ mixed oxide was active for lube oxidation. Among these materials, the sample prepared by the SC method showed the best catalytic activity due to the reservation of the high surface area and small particle size.

3.1.6. Micro-emulsion method

Surface and interfacial catalysis plays a key role in the integrated synthesis and construction of functional architectures particularly for nanosize thin film due to the effect of surface tension and viscosity [114,115]. Zhou *et al.* [116] prepared five types of CZO-modified Al_2O_3 (CZA) by SG, ME, CP with super-

Fig. 4. (a) The schematic diagram for the preparation of 3DOM CZO by the colloidal crystal template method; (b) SEM and (c) TEM images of a representative 3DOM $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$. Inset: (b) an enlarged area of 3DOM $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$, (c) the corresponding SAED pattern.

critical drying (CPS), CP with common drying (CPC), and impregnation (IM) methods and investigated the effect of preparation method on the properties of CZA. The results revealed that CZA prepared by CPS and ME methods exhibited better textural and structural properties as well as better reducibility, which led to the higher catalytic activity and wider air-to-fuel operation window of the corresponding Pd-only three-way catalysts. Boutonnet *et al.* [117] adopted a novel and direct approach for the preparation of inorganic NPs by an oil-in-water (o/w) ME method, in contrast to the typical water-in-oil ME method. As shown in Fig. 5, the strategy involves the use of organometallic precursors, which are dissolved in oil droplets in a nanometer scale (stabilized by surfactant) and dispersed in a continuous aqueous phase.

3.1.7. Self-assembly method

The self-assembly method refers to structure units such as molecules or NPs integrating spontaneously via non-covalent bonds to form aggregation with thermodynamically stable structure. The driving force of this process contains the electrostatic force, hydrogen bond, electronic effect, van der Waals force, and space effect of functional groups [118]. The self-assembly materials are all with ordered structure and morphology, and the formation process is according to the principle that free energy should be minimized and without extra external force. Chane-Ching *et al.* [119] developed a two-step self-assembly approach for the preparation of ordered 2-D or 3-D nanostructured materials with a large surface area. Ceria NPs were functionalized by using the $\text{CH}_2\text{CH}_2\text{O}$ groups of the surfactant. According to the cooperative self-assembly of colloidal NPs, hexagonal arrays of CeO_2 were obtained and the symmetry of the arrays was maintained upon heating up to 500 °C. Chou *et al.* [120] facilely synthesized a series of mesoporous CZO nanocrystallite with excellent thermal stabilities through the EISA strategy. Fig. 6 exhibited the orderedly mesoporous structure for as-prepared different Ce/Zr ratio materials.

3.1.8. Sonochemical synthesis method

Sonochemical process has proved to be an effective method for the preparation of novel materials with unusual properties [121]. Moreover, it is an environmentally friendly synthesis route for functional materials and may be a good approach that can be used to synthesize nanoporous transition metal oxide solid solutions. Nevertheless, only a few studies on sonochemical synthesis of multicomponent materials have been found.

Fig. 5. Strategies for the preparation of inorganic nanosize CZO by the o/w microemulsion reaction approach. (a) Mixing two microemulsions of identical composition except for reactants A organometallic precursor and B precipitating/reducing/oxidizing agent; (b) Using a microemulsion containing reactant A, and then directly adding reactant B. Reprinted from [117] with permission.

Gurav *et al.* [122] investigated the sonochemical synthesis of nanoporous ceria and CZO with high surface area via high-intensity ultrasound irradiation. Zhang *et al.* [123] prepared nanosize CZO with a very big surface area of 226 m²/g and average size about 3.7 nm by a sonochemical method in the presence of polyethylene glycol (PEG). Moreover, its surface area and nanosize rarely changed after being calcined at 500 °C. Recently, Nikitenko *et al.* [124] prepared $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ nanocrystallite mixed oxide with external mesopores using simultaneous sonohydrothermal treatment. The obtained material exhibited higher surface area than the similar material prepared by an ultrasonically assisted CP method.

3.1.9. Physical method

3.1.9.1. High-energy milling

The high-energy milling method relies on the high pressure and mechanic force to make particles with high density of lattice defects, and thus the as-prepared materials possess high OSC. Trovarelli *et al.* [125] synthesized nanosize CZO via

Fig. 6. TEM images of Mn-Ce_xZr_{1-x}O₂ with different Ce/Zr ratios by calcination at 600 °C. (a) Mn-Ce_{0.2}Zr_{0.8}O₂; (b) Mn-Ce_{0.4}Zr_{0.6}O₂; (c) Mn-Ce_{0.5}Zr_{0.5}O₂. Reprinted from [121] with permission.

high-energy milling, and ZrO_2 was doped into fluorite structural CeO_2 lattice when the milling speeds gradually increased. Recently, they successfully prepared CZO particles wrapped in a 2-D carbon envelope by high-energy milling of CZO powders and soot, and the atomic ratio of metal-to-carbon increased with more milling time. Consequently, the activation and transfer of the oxygen in ceria were shifted to very low temperatures, which significantly boosted the soot combustion rate [126].

3.1.9.2. Electrospinning method

The electrospinning method is a cost-effective method for preparing electrospun fibers with high surface areas and adequately small grain sizes, which are indispensable for good reducibility and fast low-temperature reoxidation in solar-driven redox cycles. The high surface area of electrospun structures can accelerate the reoxidation surface kinetics at low temperature and inhibit sintering at high reduction temperatures. Davidson and Jackson prepared a series of CZO fibers with a uniform diameter by a controlled electrospinning method [127]. The electrospinning set-up was shown in Fig. 7. These CZO fibers exhibited remarkable sinter-resistance, which maintained their structure even after 108 redox cycles with reduction at 1400 °C and oxidation with CO_2 at 800 °C. It was higher than those observed for other ceria-based materials conducting under similarly high temperature conditions.

3.1.10. Other methods

Liquid-feed flame spray pyrolysis (LF-FSP) is a facile method which was developed in recent years for material synthesis. In this synthesis strategy, organometallic alcohol solutions are usually used and are aerosolized with oxygen and ignited. The combustion process produces flames up to 1500–2000 °C. If the combustion process derived metal oxide ions are quenched rapidly enough, e.g., 1000 °C/ms, it is possible to prepare a large variety of unaggregated (easily dispersed) nanopowders whose compositions are almost completely determined by the precursors in solution [128–130]. Kim *et al.* [128] synthesized

CZO and $(\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ core-shell nanopowders by LF-FSP using metallo-organic precursors $\text{Ce}(\text{O}_2\text{CCH}_2\text{CH}_3)_3(\text{OH})$, alumatrane $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Al}$, and $\text{Zr}(\text{O}_2\text{CCH}_2\text{CH}_3)_2(\text{OH})_2$. The as-prepared materials possessed mean particle size below 20 nm and specific surface area of 30–50 m^2/g and showed good catalytic activity for HC oxidation and deNO_x reaction even without co-catalyst of noble metals.

In addition, some other methods have also been developed for cerium-zirconium based material synthesis, including supercritical anti-solvents [131,132], microwave-assisted method [133–136], electrochemical deposition [137–139], microwave method [140], etc.

3.1.11. Summary of synthesis methods for nanosize cerium-zirconium-based solid solutions

To date, a great variety of methods have been developed for the synthesis of nanosize CZO, and these methods have a great impact on the properties of materials, such as specific surface area, crystal phase, redox, OSC, and thermal stability, as listed in Table 1. The preparation of nanosize CZO usually involves four steps: the synthesis of precursor, the pretreatment of precursor, the transformation of precursor into solid solutions, and post-treatment of solid solutions. At present, the primary preparation methods for nanosize CZO are CP, SG, surfactant-assisted template, hydrothermal, SC, and ME methods, and each of them possesses its feature and certain deficiencies.

The high energy ball milling method is highly costly and time consuming, and the material prepared by this method exhibits low specific surface area and OSC value. Thus, this method is rarely employed to prepare nanosize CZO. Generally, SG synthesis is a suitable method to prepare CZO with high degree of homogeneity by controlling the hydrolytic process of the precursor like alkoxide. However, it should be taken into account that when the rates of hydrolysis between the two metals are quite different, it may be difficult to simultaneously hydrolyze the both precursors. Consequently, CZO prepared by this method often exists split phase. But the homogeneity of CZO can be improved via suitable chemical modification or adding certain solvent to control the hydrolysis rate of the both precursors. The SC method is usually used to prepare nanostructural CZO by burning $\text{Ce}(\text{NO}_3)_3$, $\text{ZrO}(\text{NO}_3)_2$, oxalyl dihydrazide, and carbonyldihydrazide. Its advantage is that the samples possess high specific surface area, and the disadvantages are high cost, waste gas producing, and low OSC value. The hydrothermal method is employed to prepare CeO_2 and ZrO_2 -containing materials, and CZO prepared by this method under supercritical conditions shows good homogeneity, high OSC value, and excellent thermal stability. However, its production amount is very little. In general, the hydrothermal method is used in laboratory and not industrialized yet. The CP method is one of the common methods to prepare CZO. It uses a precipitant to transform soluble components into complex compounds and the corresponding solid solution is obtained by separation, washing, drying, and roasting. Currently, the CP method is convenient for industrial production due to its simple process, controllable condition, cheap raw materials, and low preparation cost. Nevertheless, high temperature calcina-

Fig. 7. Fiber production via electrospinning set-up. (a) Wire coil spinneret rotating through a bath of spinning solution, fibers on a rotating wire drum collector; (b) Removal of the collected fibers from the wire drum, leaving a non-woven mat of polymer and ceramic precursor fibers; (c) SEM image of the ceramic + precursor fibers. Reproduced from [127] with permission from the PCCP Owner Societies.

Table 1

Main characteristics of different synthesis methods for nanosize CZO materials.

Synthesis method	Characteristics of the method	Characteristics of the materials
Co-precipitation method	Simple synthesis process, controllable condition, cheap raw materials, and low preparation cost	An excellent mixing of the different components, surface area 20–120 m ² /g
Sol-gel method	Mild synthetic conditions, but time consuming	Existing split phase, but high surface area
Template-assisted method	Convenience, simplicity and inducing effect of various templates with special structures or morphology	Controllable size, morphology and structure as well as high surface area
Hydrothermal and solvothermal method	Direct and rapid, high temperature (100–1000 °C), high pressure (1–100 MPa)	Homogeneous, high OSC and good thermal stability
Solution combustion method	Simple, fast, but high cost and waste gas producing	Uniform crystalline particle size and high surface area but low OSC
Micro-emulsion method	Especially for nanosize thin film	Better textural and structural properties as well as better redox behavior
Self-assembly method	Cheap, fast, simple and convenient, but difficult to prepare materials with complex structure	Ordered structure and morphology
Sonochemical synthesis method	Useful technique in the synthesis of novel materials with unusual properties and environmentally friendly synthesis route for functional materials	Remarkably high surface area
High energy ball milling method	High cost and time consuming	Low surface area and OSC
Electrospinning method	Cost-effective	High surface areas and adequately small grain sizes

tion can induce a serious decrease of specific surface area of solid solution. Moreover, when precipitation is performed in water, the particles size would aggregate and grow up in the process of drying owing to the effect of surface tension. Therefore, the various preparation technologies for nanosize CZO material synthesis still need to be improved.

3.2. Morphology for nanosize cerium-zirconium-based solid solutions

As is known to all, properties and functions of CZO materials highly depend on their morphology and size. Hence, the controllable synthesis of CZO with unique morphology is significantly important [141,142]. Meanwhile, CZO with nanometer size usually possesses high OSC value and specific surface areas, which can greatly enhance the catalytic activity. Nanopowders and one-dimensional (1-D) nanostructure nowadays have been the most popular realm of synthesis of cerium-zirconium-based materials, including nanowires, nanobelts, nanorods, and nanotubes. Moreover, nanoplates, nanodisks, linearly-mesoporous structure (two-dimensional, 2-D), and nanocages, or 3-D mesoporous or macroporous structure (three-dimensional, 3-D) and various specific morphology of CZO have also arouse the interests of researchers. CZO can be divided into five categories according to the different morphology: nanopowders, 1-D, 2-D, 3-D, and other morphology such as core-shell structure, as shown in Table 2.

3.2.1. Nanopowders

Nanopowder is an important part of the nanomaterial family, which is composed of NPs with the size of 1–100 nm. Nanopowder is a transition state between atoms (or molecules) and macroscopic objects. The quantitative change of NPs may lead to the remarkable change of material properties. In fact, the crystal symmetry, space lattice, defects, dislocations, and crystal boundaries of macroscopic objects have been deeply and systematically investigated. Nanopowders may be a prom-

ising material in both fundamental research and application development due to its special properties. Especially, CZO nanopowders have attracted much attention in recent years [143,144]. They are synthesized mainly via CP, hydrothermal, and SG methods. Despite of many studies on the synthesis technique of CZO nanopowders, it is still a tough issue to obtain products with high stability and uniform size.

To prepare nanopowders with high stability, surfactants are employed in synthesis processes to promote the dispersion of precursors. PVP (polyvinylpyrrolidone) can be used in different dispersion systems as a stabilizer agent for preventing reaction product aggregation. Si *et al.* [145] used Ce(NO₃)₃·6H₂O as precursor and PVP as stabilizing agent in alcohol solution to prepare CeO₂ colloidal particles with sizes of ca. 4 nm. Du *et al.* [146] used CTAB as template to induce the assembly of Ce_{0.7}Zr_{0.3}O₂ nanopowders via the CP method. Under the condition of plentiful reaction and aging time, CZO with a pure crystal phase was obtained. The as-prepared material possessed an average size of 15 nm, pore diameter of 2–4 nm, and specific surface area of 179 m²/g and showed high stability. Liu *et al.* [147] prepared a series of Ce-Zr-Pr nanopowder oxide catalysts via uniting solution-combustion and rotating evaporation techniques. The catalysts exhibited a cubic fluorite structure with particle sizes in the range of 6–8 nm. Darr *et al.* [143] prepared La- and Y- doped nanosize CZO with different compositions by a hydrothermal method. Both samples showed an average particle size of 4.5 nm. For nanopowder synthesis, the raw material utilization is usually inefficient and the process of preparation may also be not environmentally friendly. Thus, seeking for the efficient and comfortable synthesis of CZO nanopowders of regular morphology with high stability and activity is an imperative issue.

3.2.2. 1-D cerium-zirconium-based solid solutions

3.2.2.1. Nanowires, nanobelts, and nanofibers

Nanowires, nanobelts, and nanofibers are 1-D nanostuc-

Table 2

Main characteristics and synthesis methods of nanosize CZO materials with the different morphology.

Morphology		Synthesis method	Characteristics
0-D nanomaterials	Nanopowders	Co-precipitation, hydrothermal and sol-gel method	Particle sizes of 1–100 nm
1-D nanomaterials	Nanowires	Sol-gel, hydrothermal method	Ultrasmall diameter of ~1 nm and a length of 70 nm
	Nanobelts	Electrochemical deposition	Ultrathin
	Nanofibers	Electrospinning, hydrothermal, co-precipitation,	Uniform size from 300–400 nm in length
	Nanorods	Template-assisted method hydrothermal (sol-vothermal), ME, template-assisted method	10–40 nm in diameter and 30 nm to 2 μ m in length
	Nanotubes	Template-assisted and hydrothermal method;	~15 nm in wall thicknesses and 100 nm to 8 μ m in length, high surface areas
2-D nanomaterials	Thin film	One-step, sol-gel, template assisted hydrothermal method	Highly thermal stability
3-D nanomaterials	Nanocages	Hydrolysis process	Controlled shapes, sizes and high surface areas
	Mesoporous materials	Self-assembly, co-precipitation, hydrothermal synthesis and hard template method	High surface area and special porous structure
	Macroporous materials	Template-assisted method	Ordered macroporous materials with controlled pore size
	Hierarchically porous materials	Dual-template assisted colloidal crystal templating method	High surface area, controllable composition, thermal and chemical stability, high porosity
Other nanomaterials	Flower-like nanostructures	Electrodeposition and template-assisted hydrothermal method	Flexibility in controlling the sizes, shapes, and compositions
	Core-shell structure	Sol-gel and chemical deposition method	

tures, but studies on the morphology of CZO materials are not sufficient compared with nanopowders. Despite of this, some work has been reported. Song *et al.* [148] prepared CZO nanofibers via an electrospinning technique. In this process, P123 and polyethylene oxide (PEO) were used as co-template agents and ceric nitrate and zirconium nitrate as precursors. P123 and PEO mixture allowed the formation of microphase domains during the electrospinning process. A handful of PVP was also introduced to control the viscosity of the composite solutions for better electrospinning. The as-prepared material has a uniform size of 300–400 nm in length. Li *et al.* [149] synthesized ceria-based nanobelts by electrochemical deposition on Cu substrates. The surface morphology was highly dependent on the additive and current density of electrochemical deposition, and this method could be applied to prepare other nanosize rare earth oxide materials. Hyeon *et al.* [150] fabricated ceria nanowires with a length of 71 nm and an ultrasmall diameter of 1.2 nm by a nonhydrolytic sol-gel method. During the thermolysis of the precursor complexes, the selective adsorption of capping ligand onto particular crystallographic facets was important for the formation of ultrathin nanowires, whose lengths were tunable by altering the amount of oleylamine. This strategy is effective in adjusting the length/diameter ratio of nanowires.

3.2.2.2. Nanorods

A number of pure CeO₂ nanorods have been synthesized via hydrothermal (solvothermal), ME, template-assisted, and chemical vapor deposition methods. However, compared with the synthesis of CeO₂ nanorods, CZO nanorods are more difficult to fabricate. Du *et al.* [151] synthesized nanorod-like Ce_{0.7}Zr_{0.3}O₂ solid solutions by a sodium dodecyl sulfate-assisted precipitation method. Typical Ce_{0.7}Zr_{0.3}O₂ nanorods were 450 nm in length and 40 nm in average diameter, with specific surface area and OSC of 194 m²/g and 374 μ mol/g, respectively.

Shen *et al.* [152] prepared Ce_{1-x}Zr_xO₂ (0 ≤ x ≤ 0.2) nanorods with an average length of ~40 nm and a mean diameter of ~8 nm by an aqueous-phase CP method. The reaction was under the conditions of 95 °C in the solvent media and lasted for 8 h. Lee *et al.* [153] employed a two-step route under hydrothermal conditions and prepared CZO nanorods with average diameter and length in a range from 20–30 to 100–200 nm, respectively. Shi and Zhang *et al.* [154] designed the synthesis of MnO_m/CZO nanomaterials and investigated the effect of the morphology of CZO on the catalytic activity of MnO_m/CZO for the SCR of NO with NH₃. Three different shapes of CZO nanomaterials such as nanorods, nanocubes, and nanopolyhedra were prepared by a hydrothermal method and the temperature was maintained at 100 °C for nanorods. Zhang *et al.* [155] prepared Ce_{0.9}Zr_{0.1}O₂-supported manganese oxides (MnO_m) nanorods through a hydrothermal method with the reactants at 100 °C for 24 h. TEM images in Fig. 8 showed Ce_{0.9}Zr_{0.1}O₂ nanorods with a length range of 15–90 nm and a uniform diameter (11 ± 3 nm).

Many metal-doped CZO samples were also investigated by researchers. Dai *et al.* [156] prepared Ce_{0.6}Zr_{0.3}Y_{0.1}O₂ (CZY) solid solution nanorods with cubic fluorite structure by adopting the strategy of CTAB-assisted hydrothermal treatment at 120 and 160 °C for 72 h. Fig. 9 shows that both samples exhibited a rodlike shape with length variation from 30 nm to 2 μ m and uniform diameters of ~10 nm, and the samples contained some irregular NPs. Yan *et al.* [157] synthesized monodisperse and large-scale Pr-doped ceria nanorods by combination of low-temperature aging and high-temperature precipitation without further sintering. The morphology of the products was 400 nm in length and 30 nm in diameter, and Pr-doped ceria nanorods exhibited relatively high specific surface area (153 m²/g).

3.2.2.3. Nanotubes

Fig. 8. TEM images of (a) $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ and (b) $\text{MnO}_x/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ nanorods. HRTEM image (c) and EDS pattern (d) of $\text{MnO}_x/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ nanorods. Reprinted from [155] with permission.

Fig. 9. SEM (a,d) and HRTEM (b,c,e,f) images as well as their SAED patterns (insets) of (a–c) CZY-CTAB-120 and (d–f) CZY-CTAB-160. Reprinted from [156] with permission.

Nanotube research has become a hot spot in the material science field because of several reasons [158–160]. First of all, nanotubes with sufficient small dimensions possess high specific surface areas, good atomic efficiencies, rapid response to reaction conditions, and high activities in catalyst systems. Secondly, the tubular nanostructure may endow itself additional advantages, such as high thermal and chemical and structural stability. Finally, these structures may lead to completely new applications in nanotechnology, for example, if the nanotubes can be aligned. CZO nanotubes can be prepared via template (CNTs, polycarbonate, etc.)-assisted and hydrothermal methods. Fuentes and Baker *et al.* [161] synthesized CZO nanotubes with CeO_2 contents of 50 mol%, 70 mol%, and 90 mol% using polycarbonate membrane with pore diameter of 800 nm as template. The obtained nanotubes were 1–8 μm in length, 500 nm in diameter, and 20 nm in wall thicknesses, as shown in Fig. 10. Lee *et al.* [162] prepared zirconium-doped ceria nanotubes by mixing $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and zirconium dioxide powder in NaOH solution under hydrothermal conditions. The influence of zirconium on the growth of ceria nanotubes was also investigated, and the Kirkendall effect would affect the formation of nanotube structure. They reported a straightforward synthesis method of CZO nanotubes with high yield, several hundred nm in length, ~ 52 nm in average pore size, and 76

Fig. 10. SEM images of (a, b) $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, (c–f) $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$, and (g–i) $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ at low magnification, showing the high yield of nanotubes; at intermediate magnification, showing the structure of individual nanotubes, including several tubes viewed end-on; and at high magnification, showing the nanoparticulate nature of the nanotube walls. Reprinted from [161] with permission.

m^2/g in specific surface area. Moreover, the nanotubes possessed inner diameter ranging from 30 to 50 nm, and wall thickness was about 15 nm.

3.2.3. 2-D cerium-zirconium-based solid solutions

Sanchez *et al.* [163] prepared a highly linearly mesoporous CZO thin film with 2–4 nm pores by a one-step method. This kind of material exhibited highly thermal stability, which still retained their structural integrity even after crystallization and thermal treatment at 700 $^{\circ}\text{C}$. Niklasson *et al.* [164] fabricated CZO films by the SG method. Cerium nitrite together with zirconium oxychloride was dissolved in ethanol to prepare precursor solutions. Veszelei *et al.* [165] prepared CZO films by reactive direct current magnetron cosputtering. The films could remain completely transparent under repeated Li^+ and electron insertion/extraction and were, therefore, of much interest as counter electrodes in transparent optoelectronic devices such as smart window. Brezesinski *et al.* [166] synthesized mesostructural thin films of CZO using a novel type of amphiphilic block copolymer as template, and the films possessed highly crystallized pore walls and ordered arrays of mesopores. Zelcer *et al.* [167] adopted a straightforward and reproducible way to prepare $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($0 \leq x \leq 0.5$) thin films with linearly mesoporous structure. $\text{Zr}(\text{PrO})_4$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ were used as the inorganic sources, acetylacetone as stabilizing agent, and F127 as pore template. Janek *et al.* [168] reported a series of ordered mesoporous thin films of CZO with 17 nm diameter pores and nanocrystallite walls. The mesoporous oxide films were thermally stable and still kept their structure up to 600 $^{\circ}\text{C}$.

Dai *et al.* [156] synthesized a bowknot-like $\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_2$ entity, consisting of a variety of nano- and microslices with 2–6 μm in width and 5–10 μm in length, by adopting the strategy of P123-assisted hydrothermal treatment. These nano- and microslices were aligned along the reverse orientation of the center of the microbowknot, forming rather coarse surfaces of the

ends of a microbowknot.

3.2.4. 3-D cerium-zirconium-based solid solutions

3.2.4.1. Nanocages

CZO nanocages may exhibit excellent catalytic performance owing to the special morphology and may be also employed as novel nanoreactors due to the hollow structure. Li *et al.* [169] fabricated monodisperse CeO_2 spheres via a hydrolysis process, which then were employed as precursors and reacted with zirconium(IV) to prepare CZO nanocages with controlled compositions, sizes, and shapes according to a modified Kirkendall effect. Fig. 11 exhibited that the materials showed a special nanocage morphology which possessed high surface areas of $142 \text{ m}^2/\text{g}$ for nearly cubic nanocages, and $183 \text{ m}^2/\text{g}$ for spherical nanocages, respectively. Xu and Huang *et al.* [170] prepared the uniform monodisperse CZO nanocages with an apparent interior void. The diameters of the nanocages were about 80–100 nm.

3.2.4.2. 3-D mesoporous cerium-zirconium-based solid solutions

Nanocrystallite structured materials are desired in the practical applications due to their high surface area and special porous structure. 3-D mesoporous materials with high specific surface area, highly ordered channels, and narrow pore size distribution have provoked intensive interest, thus widespread application on catalysis. 3-D mesoporous Ce-based materials were reported in the 1990s. This material shows a broad arrangement of mesopores in the region of 2–8 nm with an optimal value at around 3.5–4.0 nm, and surfactants are significantly important to obtain high surface area mesoporous ceria because they can lower the surface tension of water in the pores during drying [171]. Many methods were developed to synthesize mesoporous ceria and CZO with crystallite framework, including self-assembly [97,172], direct hydrothermal synthesis [173], and hard-template assisted method [174,175].

Deshpande *et al.* [176] synthesized a series of CZO beads via a nanocasting approach by employing commercially available PS beads as templates. The as-prepared materials offered advantages of ease of handling and recovery and good flow properties. Moreover, the materials retained a high compositional homogeneity even after thermal treatment, and the surface

area after calcination at 500°C was in the range of 78–113 m^2/g . Other nanocasting techniques have also been reported that siliceous KIT-6 was employed as the template [177]. As expected, relatively high surface area was achieved ($> 163 \text{ m}^2/\text{g}$) despite of high calcination temperatures for example 550°C . And the aging temperature of the siliceous template was of importance because it was directly related to both the pore size and specific surface area of the target materials. The as-prepared 3-D mesoporous CZO was used for the complete oxidation of naphthalene and exhibited higher catalytic activity than CeO_2 . Additionally, these mesoporous CZO oxides also demonstrated a high stability. Lu *et al.* [178] synthesized mesoporous $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ solid solution via combining CP and self-assembly methods. Thereupon, the solid solution consisted of homogeneous nanocrystals with uniform mesopores of ca. 4 nm and showed highly thermal stability. Moreover, different surfactants had little influence on the mesoporous structures. Although many methods are developed, further research is still needed, which should be concentrated on how to improve the mesopore regularity and raise the tolerated maximum temperature.

3.2.4.3. Macroporous cerium-zirconium-based solid solutions

3DOM materials have attracted much attention because of their peculiar structure and wide application in photonic crystal, catalysis, and separation science. To date, the main technique for 3DOM material synthesis is the template-assisted method. Colloidal crystals are usually used to prepare ordered macroporous materials with controlled pore size. Li *et al.* [179,180] employed PS microspheres as templates and CA as complexing agent to prepare 3DOM CeO_2 via the SG method and reported the synthesis of 3DOM ZrO_2 by two steps. They prepared 3DOM carbon framework by using SiO_2 as templates, and then ZrOCl_2 was impregnated on the carbon framework. The final 3DOM product was obtained after the removal of carbon framework under a high-temperature condition.

Zhao *et al.* [99–102,181–184] carried out research on CZO with 3DOM morphology. 3DOM CZO was synthesized by the CCT method using EG-methanol solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ as precursor solution. To obtain 3DOM metal oxides, the solidification of these salts was necessary before the removal of PMMA. The heteropolynuclear complex containing cerium and zirconium ions using EG-methanol solution as solvent was formed at low temperature during the dry process, indicating that the solidification of the two salts occurred. The inorganic precursors were introduced to CCT and permeated the voids between the close-packed spheres, and condensed into a hard inorganic framework upon drying. After removal of excessive liquid, drying at room temperature for 12 h, and calcination at 550°C for 5 h, a 3DOM CZO material possessing perfect crystal phase was obtained.

3.2.4.4. Hierarchically porous cerium-zirconium-based solid solutions

Arandian *et al.* [185] reported a facile dual-template synthesis of Pt NPs supported on 3DOM-structured $\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_2$ (3DOM CZY) with nanovoid-like or mesoporous skeletons. It

Fig. 11. (a–c) TEM images of spherical CZO nanocages with different magnifications, (d–f) TEM images of nearly cubic-like CZO nanocages with different magnifications. Reprinted from [169] with permission.

was based on the use of a CTAB-assisted gas bubbling reduction route with $\text{H}_2\text{PtCl}_6/\text{NaBH}_4$ and P123 as soft template and well-arranged colloidal crystal PMMA microspheres as hard template to generate a 3DOM structure, as shown in Fig. 12. Pt/3DOM CZY catalysts possessed great utility because of their high surface area, diverse composition, crystallinity, thermal and chemical stability, high porosity, and uniform pore size distribution as well as their excellent catalytic performance for CH_4 combustion. Huang *et al.* [186] synthesized hierarchical CZO nanospheres with an outer diameter of about 90 nm by a modified approach (Kirkendall effect). The nanospheres showed uniform and monodisperse characteristic, which could be employed as effective adsorbents for arsenic removal. Yu *et al.* [187] developed a series of high-efficiency $\text{Pd}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0.2$ – 0.8) catalysts with mesoporous structures and macro-channels by a combined surfactant and CCT method. The non-interconnected macrochannels have a length of 20–60 nm and diameter of 1–2 nm. The high-magnification SEM images revealed that the walls of these macro-channels derived from the packing of fine particles. The intraparticle spacing was related well to the mesopores in the product and hence both macro and meso-textural structures coexisted in the system. Wei *et al.* [188] innovatively fabricated a series of 3-D ordered meso-macroporous PdCo/CZO catalysts by a combined CCT and EISA method, in which F127 and PMMA were used as mesopore and macropore templates, respectively. The resulting catalysts show ~ 240 nm in macropore diameter and ~ 5 nm in mesopore.

3.2.5. Other morphology

The other special morphology has been successfully synthesized and studied, such as flower-like, bowknot-like, core-shell and so on. This greatly broadened the application area of nanosize CZO materials. Li *et al.* [189] synthesized CZO flower-like nanostructures via the electrochemical deposition technique. By tailoring the electrodeposition conditions, various CZO flower-like structures were readily prepared, as shown in Fig. 13. CZO may be greatly influenced by different surfactants used. Zhang *et al.* [156] prepared a series of CZY with different morphology via hydrothermal treatment, in which P123 or CTAB surfactants were employed and the reaction time and temperature were regulated. The morphology of the as-prepared

Fig. 12. SEM images of 3DOM CZY support and $y\%$ Pt/3DOM CZY and Bulk CZY catalysts. (a) PMMA colloidal crystal; (b) 3DOM CZY; (c) 3DOM CZY; (d) 0.6 wt% Pt/3DOM CZY; (e) 0.6 wt% Pt/3DOM CZY; (f) 0.6 wt% Pt/3DOM CZY. Reprinted from [185] with permission.

Fig. 13. SEM images of CZO flower-like nanostructures prepared in solution of 0.02 mol/L $\text{Ce}(\text{NO}_3)_3$ + 0.005 mol/L $\text{Zr}(\text{NO}_3)_4$ + 0.1 mol/L NH_4NO_3 with current density of 2 mA/cm^2 . Reprinted from [189] with permission.

products included rods, spheres, bowknot-like shape, and octahedral shape.

Core-shell structure nanosize CZO is a good material for ion conductivity. In order to introduce more conductive interfaces, Li *et al.* [190] synthesized the doped CZO core-shell nanocomposites via a simple and cost-saving SG method. Nitrates, CA, and PEG were used as the starting materials, and the compositions of the core and the shell parts were $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ and 8 mol% Sc_2O_3 -doped ZrO_2 , respectively. The grain size of core and shell was 6 and 8 nm, respectively. The core-shell nanostructure contained about 60 nm diameter core and about 20 nm thick shell. Ozawa *et al.* [191] prepared core-shell type CZO support by precipitation of CeO_2 NPs followed by heat treatment at 800 $^\circ\text{C}$ on pure zirconia surface. Li *et al.* [169] prepared $\text{CeO}_2@\text{CZO}$ nanocages with different morphology by Kirkendall effect using the colloid ceria clusters as both chemical precursors and physical templates. This approach showed great flexibility in controlling the compositions, shapes, and sizes of the solid solution.

3.2.6. Summary of cerium-zirconium-based material with different morphology

To date, nanosize cerium-zirconium-based materials with ordered space morphology have attracted much attention due to their special and remarkable physicochemical properties in different areas. The ordered morphology includes nanopowders, 1-D nanorods, nanotubes, nanobelts, nanowires and 2-D nanofilms, nanomembranes, nanoplates and 3-D nanocages, 3-D mesoporous, macroporous and hierarchical pores. In addition, many other special morphologies have been reported, and the synthesis routes and techniques are also different. Based on the nanosize morphology, space ordered structures for CZO materials have been developed for different applications. CZO materials have been widely used in heterogeneous catalysis because of their remarkable redox properties. However, as for the research of CZO materials with different morphology, some work should be still improved: (a) stability and mechanic strength of the as-synthesized materials; (b) environmentally friendly synthesis route exploring; (c) morphology dependence factors, such as reaction time, temperature, pH value, concentration of cerium and zirconium source, raw material configuration, metal doping, etc; (d) physicochemical properties of

CZO nanomaterials with different morphologies; (e) correlation among structures, morphologies, and catalytic performance of CZO nanomaterials.

4. Cerium-zirconium-based solid solutions for heterogeneous catalytic reactions

4.1. Cerium-zirconium-based solid solutions for catalytic oxidation of environmental pollutants

CZO is a common active component used for the preparation of automotive exhaust TWCs catalysts for oxidation and reduction of combustion byproducts. CO, NO_x, and uncombusted HC can be transformed into environmentally friendly forms by tailoring their oxidation states. CZO serves as an 'oxygen reservoir' in which concurrent oxidation/reduction reactions take place, either removing oxygen to create oxygen vacancies or storing it to fill the vacancies in the solid material. In most cases, CZO porous solid is supported with metal NPs (Cu, Ag, Au, Pt, Pd), which can promote oxygen transport into and out of the 'reservoir'. For CZO-supported metal catalysts, factors such as metal type, CZO particle size, Ce/Zr ratio, pretreatment conditions, preparation method, dopants, and choice of the support may affect the catalytic activities of the final catalysts [192–196].

4.1.1. CO oxidation

Although CO oxidation is a conceptually simple reaction, it is very important to meet the rigorous environmental regulations. It is also a vital reaction occurring in the preferential oxidation of CO (CO-PROX) in a hydrogen purification system connected to polymer electrolyte membrane fuel cells

[197–200]. Therefore, a great amount of work has been devoted to this aspect, as summarized in Table 3.

4.1.1.1. Effect of the material composition

The different Ce/Zr ratios markedly affect the catalytic activity of CO oxidation over CZO catalysts. Meeyoo *et al.* [94] found that CO oxidation activity was strongly dependent on Ce/Zr ratio because of the difference in phase compositions of the mixed oxides. The cubic fluorite structure mainly existed in Ce_{1-x}Zr_xO₂ (where $x < 0.5$) and tetragonal phase was found in Ce_{1-x}Zr_xO₂ (where $x > 0.5$). The former phase could be reduced easily than the latter one. Trovarelli *et al.* [201] proposed that the catalytic activities of CZO were dependent on textural properties and composition of samples. The rate of CO₂ formation under stationary conditions was almost proportional to the amount of ceria, whereas, under cyclic feed stream conditions the rate reached a maximum when CeO₂ was within the range of 50 mol%–80 mol%. Zhao *et al.* [202] reported that the zirconium-doped CeO₂-supported cobalt catalysts were more active than the pure CeO₂ and ZrO₂-supported cobalt ones (Co₃O₄/CeO₂ and Co₃O₄/ZrO₂). When the ratio was 0.85–0.95, especially 0.85, the Co₃O₄/Ce_{0.85}Zr_{0.15}O₂ catalyst exhibited much higher catalytic activity than the others.

Reddy *et al.* [203] investigated the effect of Tb, Pr, and Hf dopant cations on the structure and catalytic properties of nanosize CZO-supported Pd catalysts for CO oxidation. They found that CO oxidation activity strongly relied on the nature of the dopant cations, and Pr cation incorporating CZO exhibited the best activity when being calcined at 800 °C. The catalytic activity was closely related to the redox couples Pr⁴⁺/Pr³⁺ and calcination temperature.

Ayastuy *et al.* [204] investigated Ce_xZr_{1-x}O₂ ($x = 0$ –1.0) sup-

Table 3
Catalytic activities of nanosize CZO materials for CO oxidation.

Catalyst	Particle size (nm)	BET area (m ² /g)	Reaction conditions	T ₅₀ (°C)	Ref.
CeO ₂	—	10	2.0% O ₂ + 4.0% CO (100 mL/min, 0.08 g sample)	311	[201]
Ce _{0.5} Zr _{0.5} O ₂	4.7	84	10.2% O ₂ + 9.98% CO (50 mL/min, 0.1 g sample)	421	[203]
Ce _{0.75} Zr _{0.25} O ₂	9–10	9.6	1.0% O ₂ + 1.0% CO (50 mL/min, 0.1 g sample)	355	[103]
Ce _{0.5} Zr _{0.3} Hf _{0.2} O ₂	3.3	86	10.2% O ₂ + 9.98% CO (50 mL/min, 0.1 g sample)	384	[203]
Ce _{0.5} Zr _{0.3} Pr _{0.2} O ₂	3.5	88	10.2% O ₂ + 9.98% CO (50 mL/min, 0.1 g sample)	364	[203]
Ce _{0.5} Zr _{0.3} Tb _{0.2} O ₂	3.2	92	10.2% O ₂ + 9.98% CO (50 mL/min, 0.1 g sample)	355	[203]
Ce _{0.67} Zr _{0.33} O ₂ -Al ₂ O ₃	4.0	146	10.2% O ₂ + 9.98% CO (50 mL/min, 0.1 g sample)	387	[206]
Ce _{0.67} Zr _{0.33} O ₂ -TiO ₂	3.7	105	10.2% O ₂ + 9.98% CO (50 mL/min, 0.1 g sample)	392	[206]
Ce _{0.67} Zr _{0.33} O ₂ -SiO ₂	3.1	172	10.2% O ₂ + 9.98% CO (50 mL/min, 0.1 g sample)	507	[206]
7% CuO/CeO ₂	6–7.9	150	1.0% O ₂ + 1.0% CO (200 mL/min, 0.1 g sample)	88	[204]
5% CuO/Ce _{0.5} Zr _{0.5} O ₂	6–8	169	3.3% O ₂ + 2.0% CO + 50% H ₂ (30 mL/min, 0.1 g sample)	89	[207]
7% CuO/Ce _{0.8} Zr _{0.2} O ₂	6–7.9	90	1.0% O ₂ + 1.0% CO (200 mL/min, 0.1 g sample)	102	[204]
7% CuO/Ce _{0.5} Zr _{0.5} O ₂	6–7.9	90	1.0% O ₂ + 1.0% CO (200 mL/min, 0.1 g sample)	120	[204]
7% CuO/Ce _{0.15} Zr _{0.85} O ₂	6–7.9	76	1.0% O ₂ + 1.0% CO (200 mL/min, 0.1 g sample)	134	[204]
7% CuO/Ce _{0.9} Zr _{0.1} O ₂	—	78	1.0% O ₂ + 1.0% CO + 50% H ₂ (30 mL/min, 0.1 g sample)	62	[205]
7% CuO/Ce _{0.8} Zr _{0.2} O ₂	—	73	1.0% O ₂ + 1.0% CO + 50% H ₂ (30 mL/min, 0.1 g sample)	77	[205]
7% CuO/Ce _{0.5} Zr _{0.5} O ₂	—	65	1.0% O ₂ + 1.0% CO + 50% H ₂ (30 mL/min, 0.1 g sample)	89	[205]
8% Co ₃ O ₄ /Ce _{0.85} Zr _{0.15} O ₂	5.4–6.1	—	1.0% O ₂ + 1.0% CO + 50% H ₂ (50 mL/min, 0.2 g sample)	135	[202]
16% Co ₃ O ₄ /Ce _{0.85} Zr _{0.15} O ₂	5.4–6.1	—	1.0% O ₂ + 1.0% CO + 50% H ₂ (50 mL/min, 0.2 g sample)	119	[205]
20% Co ₃ O ₄ /meso-Ce _{0.85} Zr _{0.15} O ₂	6.8	85	1.0% O ₂ + 1.0% CO + 50% H ₂ (50 mL/min, 0.1 g sample)	108	[208]
0.8% Pd/meso-macro-Ce _{0.6} Zr _{0.4} O ₂	7.6	69	20% O ₂ + 1.0% CO + 50% H ₂ (50 mL/min, 0.2 g sample)	65	[187]

T₅₀ is denoted as temperature corresponding to 50% CO conversion.

ported copper oxide catalysts for CO oxidation and found that the catalytic activity of this system depended on the amount of active sites located at the copper-ceria interface, which decreased with increasing of ZrO_2 loading amounts particularly for $\text{ZrO}_2 > 50\%$. The optimum activity in CO oxidation was observed for the CuO/CeO_2 catalyst. Linear correlations were found for ceria-containing catalysts between pre-exponential factor and surface Ce/Cu ratio, and a compensation effect also exhibited between pre-exponential factor and E_a , as displayed in Fig. 14. Chen *et al.* [205] prepared a series of $\text{CuO/Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0.1\text{--}0.5$) catalysts for CO oxidation. The catalytic activity for CO oxidation increased with the decrease of the amount of incorporating Zr^{4+} , and 7% $\text{CuO/Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ exhibited the best catalytic activity.

It is reported that the catalytic activity of CZO is strongly influenced by the crystal structure, defects and Ce content, the degree of reducibility, and the mobility of oxygen in the bulk. Despite all these implications, inadequate textural/structural stability and mechanical strength and fall of specific surface area at high temperatures are some problems encountered in the case of unsupported CZO, because many applications require high temperatures. Stabilization of CZO on an inert support to form stable and active catalysts is an effective way to overcome these drawbacks. Reddy *et al.* [206] synthesized CZO dispersed over Al_2O_3 , SiO_2 , and TiO_2 by the CP method and studied the influence of various supports on the thermal stability, OSC, and CO oxidation activity. Al_2O_3 -supported CZO showed the best performance, followed by TiO_2 - and SiO_2 -supported systems. The OSC properties exhibited a strong influence on the catalytic performances of ceria-based nanocomposite oxides for CO oxidation.

4.1.1.2. Effect of the pore structure

The different pore structure of CZO affects the dispersion of active species of reactant molecules and the diffusion. Luo *et al.* [207] synthesized a series of mesoporous CuO/CZO catalysts to be investigated for CO oxidation. Mesoporous CuO/CZO was much more active than non-mesoporous CuO/CZO in CO oxidation because of its higher oxygen vacancy concentration and

structural defects, larger surface area ($181 \text{ m}^2/\text{g}$) and better chemical homogeneity. Zhang *et al.* [208] prepared a series of $\text{Co}_3\text{O}_4/\text{meso-Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0.75\text{--}1.0$) catalysts using cationic surfactant CTAB and anionic surfactant ammonium dodecylbenzenesulfonate as structure-directing agent. $\text{Co}_3\text{O}_4/\text{meso-Ce}_{0.85}\text{Zr}_{0.15}\text{O}_2$ catalysts showed an outstanding catalytic activity for CO-PROX reaction. Moreover, compared to the conventional $\text{Co}_3\text{O}_4/\text{CZO}$ catalysts with the same composition [202], $\text{Co}_3\text{O}_4/\text{meso-CZO}$ with orderly mesoporous architecture displayed higher CO oxidation activity and CO_2 selectivity, which should be due to the presence of mesoporous structure affecting the cobalt oxide dispersion and redox behavior of catalyst. Yu *et al.* [187] reported a series of meso- and macroporous $\text{Pd/Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0.2\text{--}0.8$) catalysts using the surfactant template-assisted method. The meso-macrostructural $\text{Pd/Ce}_x\text{Zr}_{1-x}\text{O}_2$ showed a higher CO oxidation activity than that with mesochannel structures and the one prepared by the CP method due to the high homogeneity of crystal phase, more oxygen vacancies available, and large specific surface area.

4.1.1.3. Mechanism of CO oxidation over ceria-zirconium-based solid solutions

Liu *et al.* [209] reported that Zr was not effective for CO oxidation reaction. Yang *et al.* [210] and Tang *et al.* [211] revealed that Zr had almost no influence on the electronic structure of ceria. Therefore, CeO_2 has been widely used to represent CZO for simplicity to investigate the reaction mechanism that CO oxidation involved. A detailed CO oxidation mechanism over CZO was proposed by Trovarelli *et al.* [212]. It is supposed that CO_2 chemisorption should be statistically favored on CeO_2 rather than on CZO mixed oxides due to its more Ce^{3+} sites. In fact, ZrO_2 can only weakly adsorb CO or CO_2 and usually is not capable of forming stable carbonates. Moreover, preferential adsorption on pure CeO_2 could also be dependent on the properties of the adsorption sites. Furthermore, it was reported that the most stable surface for polycrystalline high surface area ceria was (111) among the three low index surfaces, namely CeO_2 (111), (110), and (100). After reduction this surface re-

Fig. 14. (A) Linear dependency of $\ln A_0$ with catalyst composition (Ce/Cu ratio); (B) Constable-Cremer plot for CO oxidation over $\text{CuO/Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts. Reprinted from [204] with permission.

laxed with a vacancy association mechanism. This mechanism could account for highly unsaturated sites onto which CO_2 would be preferentially adsorbed. Vacancy association had lower probability to occur in CZO due to the higher mobility resulting from the addition of a smaller cation in the lattice. Finally, zirconia could stabilize other surfaces with reactivity characteristics different from those of the (111) plane. The following five steps were proposed to account for CO oxidation reaction (Eqs. (5)–(9)):

Among which, the initial two steps accounted for CO oxidation. In Eq. (5), CO_2 entered gas phase, while Eq. (6) accounted for the adsorption of CO_2 as carbonate-like species. The rate of the two competing steps determined the intensity and the ratio of the two peaks, which were strongly dependent on the composition and specific surface area of the oxide. Eqs. (7)–(9) expressed the phenomena observed during the second half of the cycle: oxygen adsorption during the second half cycle was expressed in Eqs. (7) and (8), and reaction (9) was the reoxidation step. Moreover, it was assumed that Eq. (8) was the rate-limiting step in the oxygen dissociative adsorption process, while Eq. (7) was instantaneous. Thus, the rates of Eqs. (7) and (9) determined the observed time lag between oxygen consumption and CO_2 release.

4.1.2. NO oxidation

NO oxidation to NO_2 under O_2 -rich condition is attracting more and more attention as it is involved in many diesel de-pollution processes such as: (a) NSR strategy, where a noble metal/alkaline-earth oxide component accomplishes NO_x storage and the subsequent reduction to N_2 by adding a reducing gas in the exhaust [213]; (b) NO_2 -assisted soot combustion, where NO_2 initiates and continues along with O_2 to promote soot oxidation even under loose contact between catalyst and soot [214]; and (c) SCR of NO_x , where NO_x are selectively reduced in an O_2 -rich environment. CZO showed extremely attractive as possible substitutes of noble metals for catalytic

applications where NO oxidation to NO_2 must be accomplished [215].

4.1.2.1. Effect of the support composition

Among the various physicochemical properties, the surface composition appears to be the most relevant one influencing the NO oxidation capacity of CZO. García-García *et al.* [216] prepared two CZO with a ceria-rich and zirconia-rich surface, respectively. They found that the phase composition seemed not to be the direct factor affecting the catalytic activity for NO oxidation (as shown in Fig. 15), and that the formation of a proper solid solution prevented important surface segregation of Zr upon calcination at high temperature.

Zhong *et al.* [217] reported Cr/CZO NPs with nonuniform dopant concentration of Ce and Cr enriched on the surface as NO oxidizing catalysts. Nonuniform dopant concentration promoted the utilization of Ce and Cr, and the strong polar ability of Zr in the aqueous solution made it become the nucleation site in the hydrolysis process, resulting in Ce enriched on the surface. The adsorption of Cr by the porous structure of CZO during the impregnation resulted in nonuniform. Zr-rich sample with tetragonal structure was favorable for the increasing of surface area and the decreasing of particle size and led to a higher adsorption capacity of NO and O_2 than Ce-rich sample.

4.1.2.2. Effect of the different preparation conditions

Zhong *et al.* [218] prepared the rigid benzene-muti-carboxylate ligand-modified Cr/CZO for NO oxidation. The catalyst prepared with cinnamic acid as precipitant exhibited a larger specific surface area, a lower band gap, and a stronger ability to adsorb reactant gas. By contrast, Cr/CZO synthesized with terephthalic and trimesic acid was unbeneficial for the preparation of CZO owing to the long distance between the carboxyl groups. Subsequently, they studied the effect of precursor solution of cinnamic acid as complex ligand for the preparation of Cr-doped $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ on the oxidation activity of NO [219,220]. The solvent with appropriate polarity could decrease the band gap of the catalysts and benefit for more generation of Ce^{3+} and Cr^{6+} on the catalyst surface, which was beneficial to the adsorption of NO and O_2 . Moreover, Zhong *et al.* [221] synthesized Co/CZO using citrate acid as complexing agent and by an impregnation method. The sample pre-

Fig. 15. NO_2 production profiles during TPR experiments for $\text{NO} + 1/2\text{O}_2$ reaction. (a) Ceria-rich catalysts; (b) Zirconia-rich catalysts. Double arrow (as symbol): NO_2 . Reprinted from [216] with permission.

pared by the former method showed better catalytic performance for NO oxidation than that synthesized by the latter one due to its lower crystallite size, higher content of Ce³⁺, and easier reducibility.

4.1.3. Volatile organic compounds (voc) elimination

VOC emitted from a large diversity of sources, such as transport and industrial processes as well as household products, are identified as main contributors to air pollution either through their toxic nature and/or as precursors of ozone and photochemical smog [2,222]. Catalytic oxidation is one of the most useful and economically feasible techniques for the oxidation of VOC into CO₂, H₂O, and other less harmful compounds [223,224]. Compared to CO, NO, and CH₄ oxidation, fewer studies were devoted to VOC elimination over CZO. It is rather surprising if one considers their very good activity in oxidation reactions. The performance of CZO in eliminating hydrocarbons (alkanes, alkenes, aromatics), alcohols and other oxygenates,

and finally miscellaneous compounds will be successively reviewed below, and the results are listed in Table 4.

4.1.3.1. Alkanes

4.1.3.1.1. CH₄ oxidation

Catalytic combustion of CH₄ is an important technology for energy production and environmental pollution abatement. CZO-supported noble metals and transition metals have been widely investigated for CH₄ oxidation [48,225,226].

(a) Effect of different Ce/Zr ratio

Meeyoo *et al.* [227] prepared highly uniform Ce_{1-x}Zr_xO₂ ($x = 0-1.0$) materials via urea hydrolysis for CH₄ combustion. The incorporation of Zr into CeO₂ lattice promoted the reductive behavior. The CH₄ combustion activity of the mixed oxides was closely related to the Ce/Zr ratio, and Ce_{0.75}Zr_{0.25}O₂ showed the highest activity for CH₄ combustion with T_{50} about 540 °C. Luo *et al.* prepared Ce_xZr_{1-x}O₂-supported PdO catalysts ($x = 0-1.0$)

Table 4
Catalytic activities of VOCs combustion over nanosize CZO materials.

Catalyst	BET area (m ² /g)	Reaction conditions	T_{50} (°C)	Ref.
Ce _{0.75} Zr _{0.25} O ₂	108	2.0% CH ₄ + 21% O ₂ (100 mL/min, 0.1 g sample)	540	[227]
Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	69	2.0% CH ₄ + 20% O ₂ (125 mL/min, 0.25 g sample)	671	[185]
3DOM Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	94	2.0% CH ₄ + 20% O ₂ (125 mL/min, 0.25 g sample)	590	[185]
7% Mn/Ce _{0.67} Zr _{0.33} O ₂	62	1.0% CH ₄ + 4% O ₂ (100 mL/min, 0.5 g sample)	525	[234]
8.0% Fe ₂ O ₃ /Ce _{0.67} Zr _{0.33} O ₂ -Al ₂ O ₃	164	1.0% CH ₄ + 4% O ₂ (50 mL/min, 0.2 g sample)	520	[232]
30% Co ₃ O ₄ /Ce _{0.6} Zr _{0.4} O ₂	172	0.3% CH ₄ + 4.8% O ₂ (50 mL/min, 0.25 g sample)	380	[233]
0.25% Pd/Ce _{0.25} Zr _{0.75} O ₂ -SiO ₂	—	2.0% CH ₄ + 21% O ₂ (10 mL/min, 0.1 g sample)	355	[229]
2.0% Pd/Ce _{0.67} Zr _{0.33} O ₂	77	2.0% CH ₄ + 20% O ₂ (100 mL/min, 0.5 g sample)	400	[229]
2.0% Pt/Ce _{0.67} Zr _{0.33} O ₂	79	2.0% CH ₄ + 20% O ₂ (100 mL/min, 0.5 g sample)	417	[229]
1.6% Pt/Ce _{0.67} Zr _{0.33} O ₂	69	1.0% CH ₄ + 4% O ₂ (100 mL/min, 0.5 g sample)	335	[234]
1.2% Pt/Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	71	2.0% CH ₄ + 20% O ₂ (125 mL/min, 0.25 g sample)	558	[185]
3DOM 1.1% Pt/Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	84	1.0% CH ₄ + 4% O ₂ (125 mL/min, 0.25 g sample)	434	[185]
0.2% Au/Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	88	5.0% CH ₄ + 8% O ₂ (10 mL/min, 0.1 g sample)	600	[230]
Ce _{0.75} Zr _{0.25} O ₂	100	0.6% C ₃ H ₆ + 21% O ₂ (100 mL/min, 0.1 g sample)	330	[242]
1.5% Ru/Ce _{0.75} Zr _{0.25} O ₂	42	0.6% C ₃ H ₆ + 21% O ₂ (100 mL/min, 0.1 g sample)	212	[242]
1.5% Pd/Ce _{0.33} Zr _{0.67} O ₂ -Al ₂ O ₃	60	0.2% C ₃ H ₈ + 2% O ₂ (500 mL/min, 0.1 g sample)	400	[235]
2% Pd/Ce _{0.2} Zr _{0.78} Y _{0.02} O ₂ -Al ₂ O ₃	62	0.3% C ₃ H ₈ + 3% O ₂ (300 mL/min, 0.6 g sample)	324	[236]
2% Pd/Ce _{0.2} Zr _{0.78} Ca _{0.02} O ₂ -Al ₂ O ₃	68	0.3% C ₃ H ₈ + 3% O ₂ (300 mL/min, 0.6 g sample)	327	[236]
2% Pd/Ce _{0.2} Zr _{0.78} Ba _{0.02} O ₂ -Al ₂ O ₃	82	0.3% C ₃ H ₈ + 3% O ₂ (300 mL/min, 0.6 g sample)	348	[236]
2% Pd/Ce _{0.2} Zr _{0.75} Y _{0.05} O ₂ -Al ₂ O ₃	65	0.3% C ₃ H ₈ + 3% O ₂ (300 mL/min, 0.6 g sample)	310	[237]
0.5% Pt/3%Ni/Ce _{0.4} Zr _{0.6} O ₂	65	0.2% C ₃ H ₈ + 1% O ₂ (30 mL/min, 0.1 g sample)	330	[238]
8% CuO/Ce _{0.8} Zr _{0.2} O ₂	163	0.44% C ₇ H ₈ + 21% O ₂ (55 mL/min, 0.1 g sample)	212	[248]
1.5% Ru/Ce _{0.5} Zr _{0.5} O ₂	163	0.1% C ₆ H ₆ + 2% O ₂ (320 mL/min, 0.2 g sample)	220	[243]
1.0% Pt/Ce _{0.5} Zr _{0.5} O ₂	43	0.07% C ₇ H ₈ + 2% O ₂ (130 mL/min, 0.4 g sample)	171	[244]
4.7% Au/Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	79	0.1% C ₇ H ₈ + 40% O ₂ (16.7 mL/min, 0.05 g sample)	218	[246]
0.9% Au ₁ Pd ₂ /Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	76	0.1% C ₇ H ₈ + 40% O ₂ (16.7 mL/min, 0.05 g sample)	190	[247]
17% Pd/Ce _{0.8} Zr _{0.2} O ₂	113	40% CH ₃ OH (50 mL/min, 0.3 g sample)	200	[251]
Ce _{0.6} Zr _{0.3} Mn _{0.1} O _x	55	1.5% C ₂ H ₅ OH + 21% O ₂ (30 mL/min, 0.25 g sample)	280	[252]
Ce _{0.24} Zr _{0.4} Mn _{0.36} O ₂	163	0.08% C ₄ H ₉ OH + 21% O ₂ (100 mL/min, 0.2 g sample)	145	[255]
5% CuO/CeO ₂ -ZrO ₂ -TiO ₂	16	0.2% C ₄ H ₈ O ₂ + 21% O ₂ (100 mL/min, 0.2 g sample)	220	[257]
4% CuCe _{0.75} Zr _{0.25} O ₇ /ZSM-5	339	0.2% C ₄ H ₈ O ₂ + 21% O ₂ (400 mL/min, 0.8 g sample)	200	[258]
Ce _{0.5} Zr _{0.5} O ₂	99	0.1% 1,2-C ₂ H ₄ Cl ₂ + 21% O ₂ (500 mL/min, 0.85 g sample)	300	[260]
sulphated-Ce _{0.5} Zr _{0.5} O ₂	98	0.1% 1,2-C ₂ H ₄ Cl ₂ + 21% O ₂ (500 mL/min, 0.85 g sample)	212	[262]
1.5% Pt/Ce _{0.5} Zr _{0.5} O ₂	41	0.1% C ₂ H ₄ Cl ₂ + 21% O ₂ (1030 mL/min, 0.87 g sample)	412	[261]
0.3% Au/Ce _{0.5} Zr _{0.5} O ₂	39	0.1% C ₂ H ₄ Cl ₂ + 21% O ₂ (1030 mL/min, 0.87 g sample)	417	[261]
Ce _{0.15} Zr _{0.85} O ₂	86	0.1% C ₂ HCl ₃ + 21% O ₂ (500 mL/min, 0.85 g sample)	385	[265]

T_{50} is denoted as temperature corresponding to 50% VOC conversion.

and investigated the effect of Ce/Zr ratio on the catalytic activity for CH₄ oxidation [228]. PdO/ZrO₂ was more active than PdO/CeO₂, and the activity of PdO/Ce_{0.1}Zr_{0.9}O₂ was similar to that of PdO/ZrO₂. However, the activity of PdO/Ce_{0.2}Zr_{0.8}O₂ catalyst decreased remarkably. As the content of Ce increased again ($x = 0.3$ – 1.0), the catalytic activity increased, and PdO/Ce_{0.5}Zr_{0.5}O₂ was the most active for CH₄ oxidation in all catalysts. Fu *et al.* [229] reported a series of $y\%$ Pd/Ce _{x} Zr _{$1-x$} O₂/SiO₂ ($x = 0$ – 1.0 , $y = 0.1$ – 1.0) catalysts for catalytic CH₄ combustion. The Ce/Zr ratio played an important role in the catalytic activity of Pd/Ce _{x} Zr _{$1-x$} O₂/SiO₂. 0.5% Pd/Ce_{0.25}Zr_{0.75}O₂/SiO₂ exhibited the most active for CH₄ oxidation in all catalysts, and T_{50} was obviously lower than the other catalysts.

(b) Effect of CZO-supported different noble metals

Dai *et al.* [230] fabricated a series of nanosize polycrystalline $y\%$ AuO_m/Ce_{0.6}Zr_{0.3}Y_{0.1}O₂ ($y = 0.2$ – 10.0) using an in-situ reduction procedure with HAuCl₄ as Au source, NaBH₄ as reductant, and PVP as surfactant. The redox property of $y\%$ AuO_m/CZY catalysts was significantly improved by the introduction of Au, and AuO_m/CZY catalysts with 0.2% Au exhibited the highest catalytic activity for CH₄ combustion, which may be ascribed to the synergistic effect between the nanosize Au and CZY nanocrystalline. Moreover, they reported a series of 3DOM Ce_{0.6}Zr_{0.3}Y_{0.1}O₂-supported high-dispersion Pt NPs ($y\%$ Pt/3DOM CZY, $y = 0.6$ – 1.7) with high surface area (84–94 m²/g) and highly dispersed Pt NPs (2.6–4.2 nm). 1.1% Pt/3DOM CZY exhibited the best catalytic performance with 90% CH₄ conversion at 598 °C (GHSV = 30000 mL/(g·h)) for CH₄ combustion. The apparent activation energy (E_a) was 64 kJ/mol for 1.1% Pt/3DOM CZY, which was much lower than that of 95 kJ/mol over Bulk CZY [188]. Bozo *et al.* [231] prepared a Ce_{0.67}Zr_{0.33}O₂-supported Pt or Pd catalyst for CH₄ total oxidation. Deposition of Pt or Pd on this support resulted in a strong increase in activity, and CH₄ oxidation took place at low temperature (200–500 °C). The Pd/Ce_{0.67}Zr_{0.33}O₂ catalyst was more active than Pt/Ce_{0.67}Zr_{0.33}O₂.

(c) Effect of CZO-supported different transitional metal oxides

Fe₂O₃/Ce_{0.67}Zr_{0.33}O₂-Al₂O₃ for CH₄ combustion was reported by Gong *et al.* [232]. The optimal loading amount of Fe₂O₃ on Ce_{0.67}Zr_{0.33}O₂-Al₂O₃ for catalytic combustion of CH₄ was 8%, and the catalyst held the highest activity and the best thermal stability. The complete-conversion temperature of CH₄ for fresh and aged samples was 515 and 565 °C, respectively. Liotta *et al.* [233] synthesized Co₃O₄/CZO containing 30% Co₃O₄ and investigated its catalytic activity on CH₄ combustion. The results indicated that Co₃O₄/CZO exhibited a slightly lower CH₄ conversion than Co₃O₄/CeO₂.

(d) Effect of Pretreatment temperatures

Liotta *et al.* [233] investigated the effect of pretreatment temperature and oxygen concentration on the light-off temperature of CH₄ combustion over a Co₃O₄/CeO₂-ZrO₂ catalyst. The thermal stability of the catalyst depended on the size of the cobalt oxide crystallites and the oxygen contents. Moreover, the ceria and ceria-zirconia played a key role in inhibiting Co₃O₄ decomposition into CoO and maintaining a good

low-temperature combustion activity by dispersing the active phase Co₃O₄. Primet *et al.* [234] investigated the thermal stability of Ce_{1-x}Zr _{x} O₂ ($0 < x < 0.53$) materials. After being aged at 1000 °C under oxygen and steam, the Ce_{0.67}Zr_{0.33}O₂ solid solution exhibited the highest thermal stability, and the Pt/Ce_{0.67}Zr_{0.33}O₂ catalyst exhibited a higher activity for CH₄ combustion than Pt/Al₂O₃. However, a deactivation on stream was observed under isothermal conditions in the range of 200–500 °C. After being aged at 1000 °C, the positive effect of Ce_{0.67}Zr_{0.33}O₂ support was no longer observed.

4.1.3.1.2. Light hydrocarbons oxidation

Cerium-zirconium-based solid solutions were also used for oxidation of other light alkanes, especially for oxidation of C₃H₈. Weng *et al.* [235] reported C₃H₈ oxidation over Ce_{0.33}Zr_{0.67}O₂ and Al₂O₃ supports and investigated the effects of the supports on the catalytic performance of Pd-based catalysts for C₃H₈ oxidation. The enlargement of the interface between Pd and support during thermal aging might lead to different Pd-support interaction. Furthermore, the light-off temperature for C₃H₈ oxidation over co-aged Pd/Ce_{0.33}Zr_{0.67}O₂ and Al₂O₃ was lower than that over the mixture of aged Pd/Ce_{0.33}Zr_{0.67}O₂ and Al₂O₃. Meng *et al.* [236] prepared a series of Pd/CZO-M/Al₂O₃ (M = Y, Ca or Ba) closed-coupled catalysts by an ultrasonic-assisted successive impregnation method for the total oxidation of C₃H₈. The introduction of Y greatly enhanced the catalytic activity of the catalysts for C₃H₈ total oxidation because of the improved dispersion of Pd species and interaction between Pd species and support, which endows Pd species with higher oxidation state. They further investigated the effect of Y loading amounts (0%, 2%, 5%, 10%) on the catalysts for C₃H₈ combustion [237]. The introduction of 5% Y greatly improved the dispersion of Pd species and promoted the catalytic performance for C₃H₈ oxidation. However, further increasing the amount of Y led to the decrease of Pd-support interaction, resulting in a slight decrease of Pd 3d_{5/2} binding energy. Therefore, the chemical state of Pd species could be influenced by Y and its amount, and the catalytic activity for C₃H₈ oxidation was also affected. Wei *et al.* [238] investigated the effect of nickel on the Pt/Ce_{0.4}Zr_{0.6}O₂ catalyst for C₃H₈ oxidation and sulfur resistance. The addition of nickel not only increased the specific surface area of the catalyst, but also enhanced its redox property. As a result, the nickel doping catalyst was more active in C₃H₈ complete oxidation. Furthermore, the introduction of nickel to the catalyst was capable of enhancing the desorption amount of sulfur species under reducing atmosphere. Thereby the sulfur resistance of the Pt/Ce_{0.4}Zr_{0.6}O₂ catalyst was improved. De Leitenburg *et al.* [239] reported a series of CZO doped with Mn and Cu solid solutions for the total oxidation of light hydrocarbons. Both MnO_m and CuO at low loading amount were dissolved into CZO lattice, which significantly influenced the reductive behavior of the catalysts by increasing the oxygen mobility, and then the catalytic activity for the total oxidation of light HC was promoted.

4.1.3.2. Alkenes

Alkene combustion was exclusively performed with C₃H₆ as

model compound. D'Itri *et al.* [240] investigated the effect of sulfation on the structural, morphological, and catalytic properties of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ solid solution. When $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ was exposed to gaseous mixtures containing 20–40 ppm SO_2 at 600 °C, the crystallite grain size grew accompanied by the loss of surface area. Additionally, the introduction of 20 ppm SO_2 into the 1100 ppm $\text{C}_3\text{H}_6 + 2\% \text{O}_2 + \text{N}_2$ reaction mixture resulted in a promoting effect on the catalytic activity of C_3H_6 oxidation over CeO_2 due to the presence of acid-base interaction between surface hydroxysulfate species and C_3H_6 .

A $\text{Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2$ -supported Pd catalyst was prepared for C_3H_6 oxidation reaction [241]. The catalytic activity of Pd/CZO was strongly influenced by the pretreatment conditions such as oxidative or reductive atmosphere. The initial activity of the Pd/CZO catalyst under the insufficient oxygen condition was equivalent to the activity under the stoichiometric condition because of the property of high OSC. The CZO support promoted the dispersion of Pd oxide particles and their OSC property, which assisted the C_3H_6 oxidation reaction.

Aouad *et al.* [242] studied the catalytic behavior of CZO and Ru/CZO calcined at 500 and 600 °C for C_3H_6 oxidation. The reactivity at both temperatures increased with increasing cerium content, and the introduction of Ru greatly enhanced the reactivity of the two solids. The both specific surface area and reductive behavior of the solids affected the catalytic reactivity. However, the reducibilities were the determinant factor in the catalytic behavior where easily reducible solids were more reactive. Ru/ CeO_2 showed the optimal catalytic performance due to its high specific surface area and amount of Ru-O-Ce species. RuO_2 clusters were formed with increasing Zr contents, leading to a decrease in their catalytic activities. When the cerium content increased in the support, a more efficient interaction was observed between cerium and ruthenium oxides. This interaction hindered the formation of RuO_2 agglomerates and led to a better dispersion of ruthenium oxides and therefore a better catalytic performance.

4.1.3.3. Aromatics

Except for the report of Zhu *et al.* [243], which deals with benzene oxidation, all authors have chosen toluene as a model compound of aromatic hydrocarbons. The effect of Pt loading amounts (0.09–1.00%) on the catalytic performance of CZO-supported catalysts in the total oxidation of toluene in air was investigated by Topka *et al.* [244]. The introduction of Pt facilitated the reduction of surface cerium and decreased the acidity of the catalysts. The catalysts with 0.59% Pt showed the best catalytic activity because of the presence of highly dispersive Pt NPs. Zhao *et al.* [245] investigated a Pd/ $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ /substrate washcoat catalyst for toluene combustion. The Pd/ $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ /substrate monolithic catalyst after being calcined at 400 °C displayed good thermal stability and highly catalytic activity, and the conversion of toluene was up to 95% at 210 °C. Dai *et al.* [246] prepared $y\%$ Au/ $\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Y}_{0.1}\text{O}_2$ ($y\%$ Au/CZY, $y = 0.4\text{--}4.7$) using the CTAB-assisted hydrothermal and PVP-protected reduction methods for the oxidation of toluene. 4.7% Au/CZY exhibited the best catalytic performance at a space velocity of 20000

$\text{mL}/(\text{g}\cdot\text{h})$, and T_{50} was 32 °C for CO oxidation and 218 °C for toluene oxidation, respectively. It should be attributed to its higher oxygen adspecies concentration, superior low-temperature reducibility, and better Au NPs dispersion. Deactivation by water vapor addition was reversible due to the competitive adsorption of H_2O and toluene as well as oxygen on the catalyst surface. E_a values (39–53 kJ/mol) obtained over $y\%$ Au/CZY were much lower than that (88 kJ/mol) over CZY for toluene oxidation. Subsequently, they prepared CZY nanorods and supported Au and Pd alloy NPs [247]. 0.9% Au₁Pd₂/CZY exhibited the best catalytic activity, and T_{50} was 190 °C at a space velocity of 20000 $\text{mL}/(\text{g}\cdot\text{h})$. The active sites might be the surface oxygen vacancies on CZY, oxidized noble metal NPs, and/or interfaces between noble metal NPs and CZY. E_a values (37–43 kJ/mol) over 0.90%–0.93% Au_mPd/CZY were much lower than that (88 kJ/mol) over CZY for toluene oxidation. Yuan *et al.* [248] prepared mesoporous CZO using the surfactant template-assisted method, and then it was used as support of CuO NPs for catalytic total oxidation of toluene. CuO/CZO catalysts exhibited a wormhole-like mesoporous structure with high specific surface area and uniform pore diameter, and CuO NPs were highly dispersive on the CZO surface. 8% CuO/ $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ calcined at 400 °C showed the best catalytic activity due to the interfacial interaction between CuO and CZO support and highly dispersive CuO NPs as well as the nature of the support.

4.1.3.4. Alcohols and other oxygenates

Methanol combustion was investigated by Ziolk *et al.* [249] over CeO_2 , ZrO_2 , and mixed CZO mesoporous oxides-supported Au and Cu. The electronic state of Au and the mobility of metals and oxygen from the support played a vital role in the combustion of methanol at low temperature. In addition, the activation temperature strongly affected the mobility of surface oxygen and the oxidation states of the cationic components, which played the role of Lewis acid sites and thereby strongly influenced the activity and selectivity of methanol oxidation. Moreover, the catalytic decomposition of methanol to H_2 and CO was another efficient route. Chen and Liu *et al.* [250,251] reported catalytic decomposition of methanol to CO and H_2 over Pd/ $\text{Ce}_{0.65}\text{Zr}_{0.30}\text{La}_{0.05}\text{O}_2$ and Pd/ $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0\text{--}0.5$). All Pd-containing catalysts exhibited high selectivity to synthesis gas, among which the methanol conversion achieved 100% at 220 °C over Pd/ $\text{Ce}_{0.65}\text{Zr}_{0.30}\text{La}_{0.05}\text{O}_2$.

The ethanol complete oxidation over $\text{Mn}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Mn}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ complex compounds was studied by Wang *et al.* [252]. T_{50} was lower over $\text{Mn}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (247 °C) than that over $\text{Mn}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (280 °C) for the fresh samples. For the aged samples, however, T_{50} over $\text{Mn}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ was lower than that over $\text{Mn}_{0.1}\text{Ce}_{0.9}\text{O}_x$ solid solution. The addition of Zr to $\text{Mn}_{0.1}\text{Ce}_{0.9}\text{O}_x$ significantly improved its thermal stability, therefore, retaining its catalytic activity for the ethanol oxidation reaction. The effect of dopants ($M = \text{Mn}, \text{Y}, \text{La}$) on $\text{MnO}_m/\text{Al}_2\text{O}_3/\text{Ce}_{0.45}\text{Zr}_{0.45}\text{M}_{0.10}\text{O}_y$ for the catalytic combustion of ethanol was investigated by Chen *et al.* [253]. The catalytic activity of the $\text{MnO}_m/\text{Al}_2\text{O}_3/\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$ monolithic catalyst was promoted by doping Mn, Y, and La into $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$.

MnO_m/Al₂O₃/Ce_{0.45}Zr_{0.45}Y_{0.10}O_{1.95} exhibited the best catalytic performance with 100% ethanol conversion temperature at 230 °C. The catalytic activity of Au versus Pt on CZO in oxidation of ethanol was compared by Gaálová *et al.* [254]. Pt catalysts were more active in ethanol oxidation than Au catalysts due to their better reductive behavior and higher amount of basic centers. On the other hand, the Au catalysts exhibited the better selectivity in ethanol oxidation.

Ce_{0.6-x}Zr_{0.4}Mn_xO₂ solid solutions were used for the butanol total oxidation [255]. The textural and redox properties were improved when Mn content increased in the material, especially for $x = 0.36$, which was the most active in the butanol oxidation because of its high surface Mn⁴⁺ concentration and oxygen mobility.

Pagadala *et al.* [256] reported a versatile reusable heterogeneous CZO/SiO₂ catalyst synthesized by a very practical C–C and C–O bond forming reaction. This catalyst was superb for benzyl alcohols oxidation under the solvent-free liquid-phase condition and was reusable with no loss of catalytic activity even after multiple cycles.

Oxidations of esters were studied over non-noble metal catalysts. Xu *et al.* [257] reported a series of CeO₂ and/or ZrO₂-TiO₂-supported copper oxide catalysts for catalytic ethyl acetate combustion. CZO-promoted TiO₂ greatly improved the dispersion of CuO phase, which then enhanced the catalytic activity and prevented the formation of by-products. The complete combustion of ethyl acetate was observed at 270 °C over a 5% CuO/CZO-TiO₂ catalyst. A series of CuCe_xZr_{1-x}O_y/ZSM-5 ($x = 0–1.0$) catalysts were reported by Dou *et al.* [258], and their catalytic performance was tested for ethyl acetate abatement. The optimal performance was obtained with the CuCe_{0.75}Zr_{0.25}O_y/ZSM-5 catalyst, which achieved total combustion of ethyl acetate at 270 °C and the onset temperature as low as 110 °C. Moreover, this catalyst exhibited remarkable stability, and no deactivation phenomenon was noted after a long-term catalytic reaction for 60 h at 270 °C. Apart from Cu-based CZO catalysts, doping other metals (Mn, Y) into CZO affected the activity for ethyl acetate catalytic combustion [259]. The Mn doping greatly increased the OSC of the oxygen-storage materials (OSMs), whereas doping Y decreased the reduction temperature of catalysts. The doping of Mn and Y combined the advantages of Mn and Y. MnO_m/Ce_{0.40}Zr_{0.40}Mn_{0.10}Y_{0.10}O_y/Al₂O₃ gave the best catalytic performance, which achieved complete conversion of ethyl acetate at 240 °C, and the temperature range between the initial conversion and complete conversion was the smallest. Mn and Y entered the lattice of CZO, which modified their textural properties and greatly improved the dispersion of MnO_m active phase on the support surface.

4.1.3.5. Chlorinated VOC and other Cl-containing compounds

Chlorohydrocarbon is one of the primary air pollutants, which has superior stability and toxicity and is emitted from various sources. Therefore, great efforts have been made to eliminate these compounds. Oxidation of chlorinated hydrocarbons (CHC) can produce HCl (Eq. (10)) or Cl₂ (Eq. (11)):

The ratio between HCl and Cl₂ can be controlled by the Deacon equilibrium (Eq. (12)):

This is an exothermic reaction ($\Delta_rH^\circ = 58.4$ kJ/mol at 350 °C). Chlorine is produced in higher concentration at low temperature. For environmental reasons, it is preferable to orientate the reaction toward HCl, more easily eliminated by soda washing. Whatever the product, HCl or Cl₂, the oxidation catalyst has to work under severe conditions, generally leading to rapid deactivation. Catalyst stability is an essential parameter for VOC oxidation processes involving chlorinated hydrocarbons. CZO plays a key role in the abatement of chloroorganics.

Gutierrez-Ortiz *et al.* [260] studied the chlorinated hydrocarbons (1,2-dichloroethane and trichloroethylene) oxidation over a series of CZO and found that the surface acidity and lattice oxygen of the catalyst were responsible for the chlorohydrocarbons oxidation. The optimum performances were achieved over the zirconia-rich system. Matějová *et al.* [261] prepared Ce_{0.5}Zr_{0.5}O₂-supported Pt and Au catalysts for the total oxidation of dichloromethane. The introduction of Pt and Au on the Ce_{0.5}Zr_{0.5}O₂ support significantly promoted the redox behavior of surface ceria particular for Pt-based catalysts, but it led to the loss of catalyst acidity. As a result, the noble metal catalysts exhibited lower catalytic performance than Ce_{0.5}Zr_{0.5}O₂ in dichloromethane total oxidation due to the decreases of acid sites for chlorinated compounds. Moreover, Pt-based catalysts showed considerably high CO₂ selectivity compared with the Ce_{0.5}Zr_{0.5}O₂ support.

Gutiérrez-Ortiz *et al.* [262] prepared a series of sulphated CZO using sulphuric acid and nitric acid for the oxidative decomposition of dichloroethane. The catalyst showed a superior catalytic activity at a reaction temperature of dichloroethane decomposition as low as 80 °C. The increased acidity of CZO was responsible for its excellent activity. Li *et al.* [263] investigated the catalytic oxidation of 2-chlorophenol over a Ru/CZO catalyst. The mobility of the lattice oxygen was significantly promoted by the addition of Ru, which greatly enhanced the catalytic activity of the catalyst. González-Velasco *et al.* [264] studied the catalytic oxidation of dichloroethane and trichloroethylene over CZO in the presence and absence of *n*-hexane. The catalytic activity of the catalyst for the chlorinated organics oxidation was dependent on the Ce/Zr molar ratio, surface acidity, and OSC of CZO. CZO exhibited higher activity than pure CeO₂ in the elimination of chlorohydrocarbons in the absence of *n*-hexane. In the presence of *n*-hexane, however, an increase in the ignition temperature was observed over CZO. Furthermore, the introduction of *n*-hexane led to the formation of H₂O in its combustion process, which was responsible for the increased selectivity to HCl.

Rivas *et al.* [265] investigated trichloroethylene oxidation over CZO prepared by the CP method. The catalyst with the most acidity displayed the highest activity. A mechanism for the

dechlorination reaction was also proposed, in which the adsorption of trichloroethylene onto catalyst surface is the rate-limiting step, in agreement with that reported by Feijen-Jeurissen *et al.* [266]. Gutierrez-Ortiz *et al.* [267] investigated 1,2-dichloroethane decomposition over $\text{Cr}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0\text{--}1.0$), and the catalytic activity changed with the zirconia content for the samples. $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ exhibited the best performance. A reaction mechanism was proposed based on the in-situ FT-IR spectra. It involved 1,2-dichloroethane dehydrochlorination on the acidic sites of the catalyst to form vinyl chloride and HCl. Then the vinyl chloride got protonation from the basic species (OH) of catalyst surface, which led to the formation of carbonium ions. Subsequently, these ions were trapped by the nucleophilic oxygen from the catalyst to form chlorinated alkoxide compound and then it decomposed to acetaldehyde. Finally, CO_2 and trace amounts of CO were formed by the conversion of acetaldehyde.

4.1.4. Soot combustion

Soot emitted from diesel engine outlets is a main constituent of air pollution. It is closely related to respiratory and cardiovascular diseases as well as skin cell alterations [268]. Therefore, stringent legislation has been implemented to limit soot content from vehicles (e.g., 0.005 g/km for soot from passenger

cars in Europe since 2009, and in China since 2018). It has imposed the utilization of catalytic technologies to satisfy the required standards [269,270]. Among the different alternatives, the entrapment of particulate from exhaust gases by diesel particulate filter (DPF) has attracted much attention in recent years [271–278]. The soot particulates can be burnt off above 600 °C, however, typical engine exhaust temperatures fall within the 180–400 °C range [277–279]. In order to overcome the limitation of alternative regeneration of DPF and prevent from the deposition of particles, oxidation catalysts are developed to improve the combustion activity of soot over DPF. Among which, CZO is efficiently used due to their high mobility of reactive oxygen species and thermal stability [273,280,281]. It is now accepted that it exhibits much higher soot oxidation rate in the presence of $\text{O}_2 + \text{NO}_2$ than that in O_2 alone. In this section, soot combustion over Ce-Zr-based catalysts is reviewed, as shown in Table 5.

4.1.4.1. Effect of support composition

The effects of specific surface area and OSC of CZO on soot combustion were investigated by Trovarelli *et al.* [280]. The surface oxygen linked to ceria played a vital role for the catalytic combustion of soot, while OSC could be important when oxidation of soot particles was carried out in the absence or

Table 5

Catalytic activities of nanosize CZO materials in soot combustion.

Catalyst	Reaction conditions	T_{50}/T_m (°C)	Ref.
$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	20% O_2 (100 mL/min)/(Cat./soot = 4, tight)	522	[285]
$\text{Ce}_{0.69}\text{Zr}_{0.31}\text{O}_2$	20% O_2 (100 mL/min)/(Cat./soot = 4, tight)	458	[275]
$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	10% O_2 (100 mL/min)/50 mg sample (Cat./soot = 9, tight)	469	[282]
$\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2\text{-NP}$	10% O_2 (100 mL/min)/50 mg sample (Cat./soot = 9, tight)	435	[283]
3DOM $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$	0.2% $\text{NO} + 10\%$ O_2 (100 mL/min) (Cat./soot = 10, loose)	388	[102]
HP $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	20% O_2 (100 mL/min) (Cat./soot = 4, tight)	415	[289]
K/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	10% O_2 (500 mL/min)/110 mg sample (Cat./soot = 10, tight)	340	[187]
Ru/K/ $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	10% O_2 (500 mL/min)/20 mg sample (Cat./soot = 20, loose)	385	[306]
Ru/K/ $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	0.05% $\text{NO} + 10\%$ O_2 (500 mL/min)/ 20 mg sample (Cat./soot = 20, loose)	393	[306]
Ru/Ba/ $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	10% O_2 (500 mL/min)/20 mg sample (Cat./soot = 20, loose)	585	[306]
Ru/Ba/ $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	0.05% $\text{NO} + 10\%$ O_2 (500 mL/min)/20 mg sample (Cat./soot = 20, loose)	495	[306]
$\text{Ce}_{0.48}\text{Zr}_{0.5}\text{La}_{0.02}\text{O}_{1.99}$	6% O_2 (400 mL/min)/25 mg sample (Cat./soot = 20, tight)	414	[284]
$\text{Ce}_{0.84}\text{Zr}_{0.15}\text{Y}_{0.01}\text{O}_2$	20% O_2 (100 mL/min) (Cat./soot = 4, tight)	456	[405]
$\text{Ce}_{0.8}\text{Zr}_{0.1}\text{Pr}_{0.1}\text{O}_2$	10% O_2 (100 mL/min)/50 mg sample (Cat./soot = 9, tight)	444	[282]
$\text{Ce}_{0.4}\text{Zr}_{0.5}\text{Pr}_{0.1}\text{O}_2$	0.2% $\text{NO} + 5\%$ O_2 (100 mL/min) (Cat./soot = 10, tight)	361	[274]
$\text{Ce}_{0.48}\text{Zr}_{0.5}\text{Pr}_{0.02}\text{O}_{1.99}$	6% O_2 (400 mL/min)/25 mg sample (Cat./soot = 20, tight)	410	[284]
$\text{Ce}_{0.48}\text{Zr}_{0.5}\text{Tb}_{0.02}\text{O}_{1.99}$	6% O_2 (400 mL/min)/25 mg sample (Cat./soot = 20, tight)	414	[284]
$\text{Ce}_{0.48}\text{Zr}_{0.5}\text{Sm}_{0.02}\text{O}_{1.99}$	6% O_2 (400 mL/min)/25 mg sample (Cat./soot = 20, tight)	411	[284]
3DOM $\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Pr}_{0.1}\text{O}_2$	0.2% $\text{NO} + 5\%$ O_2 (100 mL/min)/110 mg sample (Cat./soot = 10, loose)	361	[103]
$\text{Ce}_{0.5}\text{Zr}_{0.2}\text{Fe}_{0.3}\text{O}_2$	10% O_2 (500 mL/min)/165 mg sample (Cat./soot = 10, loose)	310	[287]
3DOM $\text{Ce}_{0.8}\text{Zr}_{0.1}\text{Fe}_{0.1}\text{O}_2$	0.1% $\text{NO} + 0.1\%$ $\text{NH}_3 + 3\%$ O_2 (100 mL/min)/110 mg sample (Cat./soot = 10, loose)	375	[182]
3DOM $\text{Ce}_{0.8}\text{Zr}_{0.1}\text{Mn}_{0.1}\text{O}_2$	0.1% $\text{NO} + 0.1\%$ $\text{NH}_3 + 3\%$ O_2 (100 mL/min)/110 mg sample (Cat./soot = 10, loose)	402	[184]
3DOM $\text{Ce}_{0.8}\text{Zr}_{0.1}\text{Co}_{0.1}\text{O}_2$	0.1% $\text{NO} + 0.1\%$ $\text{NH}_3 + 3\%$ O_2 (100 mL/min)/110 mg sample (Cat./soot = 10, loose)	433	[184]
3DOM $\text{Ce}_{0.8}\text{Zr}_{0.1}\text{Ni}_{0.1}\text{O}_2$	0.1% $\text{NO} + 0.1\%$ $\text{NH}_3 + 3\%$ O_2 (100 mL/min)/110 mg sample (Cat./soot = 10, loose)	429	[184]
Ru/ $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$	20% O_2 (75 mL/min)/11.67 mg sample (Cat./soot = 9, loose)	360	[294]
3DOM Au/ $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$	0.2% $\text{NO} + 5\%$ O_2 (50 mL/min)/110 mg sample (Cat./soot = 10, loose)	375	[101]
Cu/ $\text{Ce}_{0.55}\text{Zr}_{0.45}\text{O}_2$	9.5% O_2 (500 mL/min)/110 mg sample (Cat./soot = 10, tight)	365	[296]
Co/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	15% O_2 (35 mL/min)/100 mg sample (Cat./soot = 10, tight)	386	[298]
Ni/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	20% O_2 (60 mL/min)/100 mg sample (Cat./soot = 4, tight)	463	[299]
Ag/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$	5% $\text{H}_2\text{O} + 4.8\%$ O_2 (50 mL/min)/200 mg sample (Cat./soot = 19, loose)	286	[295]
Ag/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$	5% $\text{H}_2\text{O} + 0.1\%$ $\text{NO} + 4.8\%$ O_2 (50 mL/min)/200 mg sample (Cat./soot = 19, loose)	279	[295]
CuO-CoO/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	20% O_2 (60 mL/min)/100 mg sample (Cat./soot = 4, tight)	363	[299]
CuO-NiO/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	20% O_2 (60 mL/min)/100 mg sample (Cat./soot = 4, tight)	388	[299]

T_{50} and T_m are denoted as temperature corresponding to 50% soot conversion and temperature at the maximum CO_2 concentration in the process of soot combustion, respectively. Loose or tight is referred to that the contact condition between catalyst and soot is loose contact or tight contact.

defect of gaseous oxygen. The effects of Ce/Zr ratios on the phase composition and catalytic activities of CZO and Pr/CZO samples for soot combustion were investigated by Bensaid *et al.* [282], as displayed in Table 5. The role of Zr in stabilizing surface area of ceria was also important when evaluating the effect of composition on soot combustion activity. Fino *et al.* [283] prepared a series of nanostructured CZO with different Zr contents and structural features for soot combustion. The optimally catalytic performance was obtained for the nano-polyhedra $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ catalyst due to its higher mobility of the lattice oxygen and easier reducibility compared with other catalysts. The substitution of some Zr^{4+} ions into Ce^{4+} was favorable for the generation of defects in the ceria lattice, thereby leading to a distortion of the oxygen sublattice. Nevertheless, the amount of redox Ce species decreased with increasing Zr contents. Therefore, it seemed that the substitution of Zr for Ce did not have a direct promotion effect on the oxidation activity of catalysts.

The effect of the rare earth elements-modified CZO on the catalytic combustion of soot was investigated. Aneggi *et al.* [284] studied the effect of rare earth elements (La, Pr, Sm, Tb) on the textural and structural characteristics of CeO_2 and CZO for soot combustion. CeO_2 doped with these rare earth elements exhibited more active activities due to the increased oxygen storage, which could provide an alternative route for the oxidation of big soot particles in contact with ceria. However, CZO modified with rare earth elements did not achieve lower combustion temperature, which was comparable to CeO_2 and CZO. The role of Pr as dopant for ceria-based catalysts was studied in CO and soot oxidation by Zhao *et al.* [103]. It appeared that the incorporation of Pr species into CZO framework improved the oxidation activity for CO, while this positive effect was less prominent for soot combustion due to the effect of catalyst morphology. The phase compositions of Pr-modified CZO were similar to those of corresponding CZO samples, and cubic and tetragonal phases coexisted in the samples with moderate zirconia content, which was beneficial to soot combustion. Additionally, the effects of thermal and hydrothermal treatments on the catalytic activities of 3DOM CeO_2 , $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$, and $\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Pr}_{0.1}\text{O}_2$ for soot oxidation were comparatively studied. Compared with 3DOM CeO_2 , 3DOM Ce-Zr-based solid solutions, especially Pr-modified $\text{Ce}_{0.6}\text{Zr}_{0.3}\text{Pr}_{0.1}\text{O}_2$ solid solution, showed the highest stability due to its lowest lattice oxygen mobility among the three samples. The relative efficacy of the La promoter in CZO was investigated systematically for soot oxidation at low temperature [285]. The addition of La^{3+} to ceria promoted the oxidation rate of soot compared with pure ceria and Zr^{4+} -doped ceria. This should be due to the more active oxygen provoked by defective structure of ceria, which was induced by the presence of La^{3+} . The effect of Y doping and loading on the physicochemical properties and soot combustion activity of CZO was investigated by Bueno-López *et al.* [286]. In tight contact, $\text{Ce}_{0.85-x}\text{Zr}_{0.15}\text{Y}_x\text{O}_2$ mixed oxides on the catalytic activity with respect to yttrium. And in loose contact, the catalytic activity was dependent on their specific surface area, and catalysts $\text{Ce}_{0.85-x}\text{Zr}_{0.15}\text{Y}_x\text{O}_2$ (10–13 m^2/g) were more active than $\text{Ce}_{1-x}\text{Y}_x\text{O}_2$ (2–3 m^2/g). In this loose contact condi-

tion, the yttrium doping and loading had a minor or null effect on the activity, and the stabilizing effect of the specific surface area due to zirconium doping prevailed.

4.1.4.2. Effect of preparation method

The catalytic performances of CZO-based materials for soot combustion were influenced by the preparation method. Sang *et al.* [287] reported a series of $\text{Ce}_{0.5}\text{Fe}_{0.30}\text{Zr}_{0.20}\text{O}_2$ catalysts prepared by different methods (CP, SG, physical mixed, impregnation, and hydrothermal method). Fe^{3+} and Zr^{4+} were incorporated into ceria lattice to form a homogeneous Ce-Fe-Zr-O solid solution by the CP method, but two kinds of Fe phases existed in Ce-Fe-Zr-O catalysts prepared by other methods: dispersed Fe_2O_3 clusters and Fe^{3+} incorporated into CeO_2 lattice. The free Fe_2O_3 clusters could promote the activity of catalysts for soot combustion comparing with Ce-Fe-Zr-O solid solution owing to the synergetic effect between free Fe_2O_3 and surface oxygen vacancies. In addition, the activity of catalysts considerably relied on the surface reducibility of free Fe_2O_3 particles. The hydrothermal $\text{Ce}_{0.5}\text{Fe}_{0.3}\text{Zr}_{0.2}\text{O}_2$ catalyst displayed the minimum ignition temperature (251 °C) and maximum oxidation rate temperature ($T_m = 310$ °C) for the combustion of soot in tight contact between soot and catalysts. This was due to the both abundant free Fe_2O_3 particles and high oxygen vacancy concentration. Even after being aged at 800 °C for 10 h, T_m still displayed a low value at 361 °C.

4.1.4.3. Effect of pore structure

It is well known that the conventional ceria-zirconium-based catalysts have smaller pore sizes (< 10 nm) than soot particles (> 20 nm). Therefore, soot particles are difficult to enter the inner pores of these catalysts to access active sites. So how to effectively make use of the inner surface for increasing the contact area between catalysts and soot particles is a key factor to enhance the catalytic activity for the removal of soot. Fino *et al.* [283] investigated the soot combustion over microporous and mesoporous $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ oxides. Lower soot conversion was achieved for both microporous and mesoporous $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ with similar Ce/Zr ratio. $\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$ particle catalyst showed the worse activity than the porous materials, which confirmed the important role of the textural properties for soot combustion. 3DOM CZO contains periodic arrays of interconnected macropores [102]. The open, interconnected macroporous structure is a desirable feature for diesel soot combustion. Compared with that of disordered macroporous (DM) catalysts, 3DOM samples facilitate the contact between soot and catalysts and promote the catalytic activity for soot combustion. T_{50} of 3DOM samples could be lowered by 51 °C at most, as shown in Fig. 16. Then, 3DOM CZO-supported Au NPs catalysts were prepared via the gas bubbling-assisted membrane reduction method [288]. This kind of catalysts combined both advantages of good contact between diesel soot and catalyst by 3DOM supports and the highly active sites for the activation of O_2 by Au clusters with suitable nanosize, and they exhibited good catalytic performances for the oxidation of soot. 3DOM Au/ $\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$ catalyst showed T_{50} as low as 375 °C. In addition, Pr-modified 3DOM

Fig. 16. T_{50} of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts with different macroporous structures versus Zr molar fraction for soot combustion. Reprinted from [102] with permission.

CZO was prepared by a CCT method [103]. It was used for the removal of soot and exhibited higher catalytic activities compared with DM ones. This was due to the improved contact efficiency between soot and ordered macroporous structure.

Zaletova *et al.* [289] reported that hierarchical porous (HP) CZO was prepared using small-size fraction of wood as template for oxidation of diesel soot particulate. HP CZO exhibited higher soot conversion over regular CZO due to its larger surface area, higher amount of mobile lattice oxygen and lower temperature of oxygen release.

4.1.4.4. Effect of active phase

Ru is established as a successful catalytic system in oxidation reactions [290–293]. Nascimento *et al.* [294] reported the soot combustion over Ru-doped $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ nanopowders in the temperature range of 220–500 °C. $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ showed good tolerance to water as well as excellent thermal stability. The addition of Ru NPs (8–10 nm) to $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ greatly boosted the reactivity of the mixed binary catalyst due to the increased active oxygen species. Chen and Zheng [295] prepared a mesoporous Ag/CZO catalyst with Ag/Ce structure by the CP method using a mixture of $\text{NH}_3\cdot\text{H}_2\text{O}$ and KOH as precipitant. The Ag-Ce interaction led to the increase of Ag^+ species, which was favorable for the activation of oxygen species. In addition, it was found that Ag^0 species surrounding with Ag^+ species was more beneficial to activating the oxygen. While Ag-Ce interface brought about Ag^+ species, which would be more effective in transferring the activated oxygen species. Thus, the Ag-based catalyst with optimal Ag-Ce interaction exhibited excellent performance for soot oxidation even in the loose contact mode and in the absence of NO_x . And its activity could keep stable for several runs, which was attributed to Ag-Ce interaction along with different distribution of Ag species.

Transition metals, such as Co, Cu and, Mn, are widely used in commercial soot removal systems. Wu *et al.* [296] investigated the soot catalytic oxidation over Cu doping CeO_2/CZO catalysts. Cu modification improved the activity and selectivity of CeO_2 and CZO for the catalytic oxidation of soot attributing to the well dispersed copper oxide species strongly interacting with

the ceria surface, which might lower the activation energy of soot combustion. Reddy *et al.* [297] reported CZO-supported Cu catalysts for soot combustion. The introduction of Cu^{2+} into CZO was benefited to the formation of more structural defects, which accelerated the oxygen diffusion and induced the production of more surface-active oxygen species. It was responsible for the improved low-temperature activity of soot combustion. Chen *et al.* [298] investigated the effect of Co addition on catalytic performance of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ mixed oxide for soot combustion. The catalytic activity of the catalyst was effectively improved by the addition of Co with soot due to the existence of synergistic effect between Co and Ce. CZO-based monometallic (CoO/CZO and NiO/CZO) and bimetallic (CuO-CoO/CZO and CuO-NiO/CZO) catalysts were prepared by Reddy *et al.* [299] and used for soot oxidation. The bimetallic CuO-CoO/CZO catalyst exhibited the best catalytic activity ($T_{50} = 363$ °C) and nearly 100% CO_2 selectivity due to the formation of facile reduction and abundant oxygen vacancies as well as the small size of the metal particles and the high specific surface area. Escribano *et al.* [300] found that the Mn/CZO catalyst showed high activity for soot combustion, producing CO_2 and CO as a by-product in the temperature range of 152–452 °C, and the amount of CO decreased significantly with increasing O_2 concentration in the feed gases.

Adding low melting point metal salts can improve the catalytic activity [301], and alkali metals have been reported as a molten salt to promote catalyst-soot contact by increasing surface mobility [102,302,303]. Neyertz *et al.* [279] reported that the introduction of K promoted the catalytic performances of K/ CeO_2 /cordierite and K/ $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ /cordierite for soot combustion. However, the K/ CeO_2 /cordierite catalyst was more active due to the distribution of Zr on the surface of $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$, which decreased the catalytic activity. Zhu *et al.* [304] investigated the effect of KNO_3 loading on $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ for catalytic soot combustion. KNO_3 loading on $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ resulted in a distinct enhancement in the catalytic activity due to that KNO_3 favored the formation of chemisorbed oxygen and carbonate species (C-O-K), which could react with soot to yield CO_2 , and the reduced state C-M was reoxidized by O^* to reform C-O-K. In addition, Wu and Weng *et al.* [305] studied the role of CZO in diesel soot oxidation and thermal stability of a potassium catalyst, and they believed KNO_3 to be the key factor affecting soot catalytic combustion due to that the nitrate can act as an oxidant of soot being transformed into reduced nitrite species.

Castoldi *et al.* [306] investigated K- and Ba-doped Ru supported catalysts for the removal of soot in the presence of NO_x . 1 wt% Ru-10 wt% AM/MO (AM = Ba or K; MO = $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, ZrO_2 , Al_2O_3) catalysts promoted the soot particulate combustion in the presence of NO/O_2 . The promotion effect for K-based catalysts seemed to be not dependent on the nature of the support, and it appeared to be closely related to the synergic interaction between Ru and K that boosted the combustion of soot at low temperature. K-containing catalysts exhibited very low onset temperature, in the range 220–235 °C. In addition, all Ru-based samples were able to simultaneously remove NO_x and soot when operating under isothermal cycling conditions, i.e.,

alternating lean-rich phases based on the typical diesel engine NO_x reduction strategy. In particular, the materials showed a NO_x storage capacity comparable to that of model Pt-based catalysts. NO_x storage capacity increased over Ru-based systems in the presence of soot particulate, while for model Pt-containing catalysts a detrimental effect of soot was found. Among all the developed formulations, K-based materials exhibited higher NO_x storage capacity and higher soot oxidation activity compared to Ba-containing samples.

4.1.4.5. Mechanisms of soot combustion over nanosize ceria-zirconium-based solid solutions

The combustion of soot over ceria mainly relies on the redox couple. $\text{Ce}^{3+}/\text{Ce}^{4+}$ with its ability shifts between Ce_2O_3 and CeO_2 , which is associated with the OSC of ceria. The surface oxygen of pure ceria is used for the soot oxidation and the consecutive vacant site is quickly refilled by gaseous/subsurface oxygen. Doped ceria can create more structural defects compared to pure ceria. So, these defects facilitate either more gaseous oxygen to adsorb onto the surface or diffusion of subsurface lattice oxygen onto the surface, thereby enhancing the formation of active oxygen species. It was reported that the rate of this active oxygen transfer to soot is much faster than that of both gas phase oxygen transfer to soot. It is self recombination to give O_2 , hence plays a crucial role in the soot oxidation. The reaction mechanism for soot combustion in the presence of O_2/NO over 3DOM $\text{Au}/\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts was investigated by Zhao *et al.* [101], and they proposed a reaction pathway for soot combustion, as shown in Fig. 17. The synergic effect between Au particle and $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ support played an important role for soot combustion. So far, the accepted mechanism [285,307,308] for the catalytic oxidation of soot over cerium-zirconium-based solid solutions involved the following steps:

where M_{red} and $\text{M}_{\text{ox}}-\text{O}$ represented the reduced and oxidized states of the catalyst, respectively. Gas-O stood for the oxidant gas (O_2 , CO_2 , H_2O , etc.), C_f denoted a carbon active site or free site on the soot surface, and SOC represented a surface carbon-oxygen complex. In the first step, the catalyst “captured” oxygen from the gas-phase molecules and was itself oxidized. In the second step, the active oxygen on the catalyst trans-

ferred/spilled over to the soot and the catalyst was reduced. In the third step, the SOC decomposed to yield CO or CO_2 .

4.2. Nanosize cerium-zirconium-based solid solutions for selective oxidation of NH_3

The removal of NH_3 from waste streams is becoming an important issue due to ever increasing environmental concerns [309]. In order to control the NH_3 slip, several different techniques have been used for the elimination of NH_3 , such as adsorption, chemical treatment, catalytic decomposition, and selective catalytic oxidation (SCO) [310–314]. Among which, SCO of NH_3 to N_2 from oxygen-containing waste gases over CZO is becoming a hot issue in recent years.

4.2.1. Effect of material composition

Qu *et al.* [315] investigated SCO over $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($0.2 \leq x \leq 0.8$) mixed oxides. Compared with pure CeO_2 and ZrO_2 , CZO exhibited more acid sites and higher catalytic activity. Especially, the $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ catalyst displayed the highest NH_3 conversion and the lowest total conversion temperature up to 360 °C, which was associated with the partial phase segregations of ZrO_2 in $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$. Additionally, zirconium-rich samples ($x > 0.4$) showed the higher N_2 selectivity ($\sim 100\%$), and the formation of N_2O was the main reason resulting in the low N_2 selectivity for these catalysts ($x \leq 0.4$). They further studied Al-promoted $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ mixed oxides in the SCO of NH_3 to N_2 [316]. The addition of Al to $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ greatly improved the oxidation activity of NH_3 . Particularly, the 3% Al- $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ catalyst exhibited higher NH_3 conversion (12.7%) than the $\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$ catalyst due to the improved oxygen mobility, reducibility, and oxygen vacancies. Among these, oxygen vacancy was thought to be the essential oxygen adsorption and activation sites. Therefore, more oxygen vacancies facilitated NH_3 oxidation reaction.

4.2.2. Effect of active phase types and reaction condition

Qu and Wang *et al.* [317] prepared a series of Cu/CZO materials by the incipient-wetness impregnation, CA-SG, and homogeneous precipitation methods. Cu/CZO prepared by the CA-SG method exhibited the best NH_3 -SCO activity owing to its better adsorption capacity, more isolated Cu^{2+} , and active oxygen ad-species. The influence of Ni loading (0, 5%, and 10%), oxygen amounts ($\lambda = 0.25, 0.5$), and gas hourly space velocity (50000, 100000, and 150000 h^{-1}) on catalysts for NH_3 -SCO was investigated by Nassos *et al.* [318]. 10% Ni/ $\text{Ce}_{0.9}\text{La}_{0.1}\text{O}_2$ showed the optimally catalytic activity with 65% and 97% N_2 yield at 500 and 750 °C, respectively. Increasing λ and lowering the gas hourly space velocity led to considerably improved N_2 yield at 500 °C. Qu and Yan *et al.* [319] synthesized Ru-modified $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ for NH_3 -SCO. The 0.2% Ru-modified $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst displayed excellent performance for the SCO of slip NH_3 , and SO_2 could enhance the removal of slip NH_3 in the presence of NO_x but also slightly suppressed NH_3 oxidation and significantly improved N_2 selectivity to 100% in the absence of NO_x , as shown in Fig. 18.

Fig. 17. Mechanism illustration of soot combustion over 3DOM $\text{Au}/\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts at different temperatures in the presence of O_2 and NO . Reprinted from [101] with permission.

Fig. 18. (a) NH₃-SCO efficiency over various catalysts at 350 °C; (b) N₂ selectivity of NH₃-SCO with or without SO₂ over various catalysts. GHSV = $\sim 3 \times 10^5$ h⁻¹, temperature = 350 °C, 30 ppm of NH₃, 30 ppm of NO, 500 ppm of SO₂, the other gas including 4% O₂ and N₂. Reprinted from [319] with permission.

4.2.3. Mechanisms of NH₃ oxidation over nanosize ceria-zirconium-based solid solutions

Qu and co-worker [317] proposed that the mechanism of NH₃-SCO with lattice oxygen was different from that of gaseous oxygen, which was much less active than gaseous oxygen at low temperature. They suggested that the reaction mechanism of NH₃-SCO over Ru/Ce_{0.6}Zr_{0.4}O₂ should follow an internal SCR mechanism [319], as shown in Fig. 19, which was in accordance with the results of Breen *et al.* [320]. The adsorbed NH₃ was first activated and reacted with lattice oxygen to form a -HNO intermediate. Subsequently, -HNO reacted with O₂ to generate NO. Meanwhile, the formed NO interacted with -NH₂ to produce N₂, and N₂O as the byproduct.

4.3. Nanosize cerium-zirconium-based solid solutions for selective reduction of NO_x

Fig. 19. Mechanism of NH₃-SCO and the effect of SO₂. Reprinted from [319] with permission.

NO_x produced from the combustion of fossil fuels such as coke in the electrical power plants or petroleum in the engines of vehicles brought about ecological and health hazards [321]. The nitrous oxide N₂O, not submitted to drastic regulations as NO_x, is considered as a nontoxic greenhouse gas. However, its global warming potential is 310 times as that of CO₂, and its abatement is often considered as a priority to avoid erratic climate changes in the next decades [322,323]. Therefore, great efforts were devoted to the development of highly efficient catalysts for the elimination of NO_x including N₂O [324–326]. CZO has drawn ever increasing attention due to its specific properties. NO_x can be reduced or decomposed to N₂ by direct decomposition or by chemical reduction using reductants such as NH₃, H₂, HC, etc.

4.3.1. NH₃-SCR

NH₃-SCR is regarded as an effective method for the removal of NO_x from stationary and mobile sources, and the catalytic efficiency of this technique is significantly affected by the composition of CZO supported catalysts, as shown in Table 6.

4.3.1.1. Effect of support composition

Zhang *et al.* [327] studied the catalytic activity of the 3DOM CZO catalyst doped by metal M (Mn, Fe, Cu and Co) for NH₃-SCR of NO_x. Those dopants were well incorporated into Ce lattice, except for Cu, and the introduction of those additives to CZO enhanced the active oxygen species, surface reducibility and acidity of the catalysts. Therefore, these doped catalysts displayed better catalytic activity than CZO at low temperature. Among them, the Co-modified catalyst showed the optimum catalytic activity attributed to its highest O_α/(O_α + O_β) ratio and reducibility, as well as the strongest NH₃ adsorption ability. In addition, Fe and Mn dopants effectively broadened the activation temperature window.

The effect of nickel- and sulfate- modified CZO for NH₃-SCR of NO in the presence of excess O₂ was investigated by Weng *et al.* [328]. The addition of Ni increased the strength of Lewis acid sites of the catalyst, which was viewed as the essential active sites for low-temperature NH₃-SCR reaction. Additionally, the sulfate modification induced the formation of Brønsted

Table 6Catalytic activities of nanosize CZO materials in NH₃-SCR of NO_x.

Catalyst	Reaction conditions	X _{NO} (%)	T _r (°C)	S _{N2} (%)	Ref.
Ce _{0.75} Zr _{0.25} O ₂	NO/NH ₃ /H ₂ O/O ₂ = 0.05:0.05:5:5/300000 h ⁻¹	77	300–350	—	[346]
3DOM Ce _{0.8} Zr _{0.2} O ₂	NO/NH ₃ /SO ₂ /O ₂ = 0.05:0.05:0.02:3/20000 h ⁻¹	>90	275–425	—	[327]
3DOM Ce _{0.75} Zr _{0.2} M _{0.05} O _{2-δ} (M = Fe, Cu, Mn, Co)	NO/NH ₃ /SO ₂ /O ₂ = 0.05:0.05:0.02:3/20000 h ⁻¹	>90	225–450	—	[327]
Ni _{0.04} Ce _{0.81} Zr _{0.15} O ₂	NO/NH ₃ /H ₂ O/CO ₂ /O ₂ = 0.05:0.05:10:14:14/160000 h ⁻¹	40–50	275–375	81	[328]
Ni _{0.04} Ce _{0.81} Zr _{0.09} SO _{0.06} O ₂	NO/NH ₃ /H ₂ O/CO ₂ /O ₂ = 0.05:0.05:10:14:14/160000 h ⁻¹	>80	275–425	—	[328]
Mo _{0.5} CeZr ₂ O _x	NO/NH ₃ /O ₂ = 0.05:0.05:5/50000 h ⁻¹	>90	220–425	—	[338]
10% P/Ce _{0.75} Zr _{0.25} O ₂	NO/NH ₃ /H ₂ O/O ₂ = 0.05:0.05:5:5/300000 h ⁻¹	>80	300–500	—	[346]
10% P/Ce _{0.75} Zr _{0.25} O ₂	NO/NH ₃ /O ₂ = 0.05:0.05:5/30000 h ⁻¹	>80	250–450	—	[347]
ZP/Ce _{0.75} Zr _{0.25} O ₂	NO/NH ₃ /H ₂ O/O ₂ = 0.05:0.05:5:5/300000 h ⁻¹	>80	240–470	—	[346]
F/Ce _{0.5} Zr _{0.5} O ₂ /TiO ₂	NO/NH ₃ /O ₂ = 0.06:0.06:6/71400 h ⁻¹	>80	290–450	—	[330]
9.1% WO ₃ /Ce _{0.75} Zr _{0.25} O ₂ (x = 0.58, 0.4)	NO/NH ₃ /H ₂ O/CO ₂ /O ₂ = 0.05:0.05:10:10:10/160000 h ⁻¹	>90	275–500	100	[335]
5% Mo/Ce-ZrO ₂	NO/NH ₃ /O ₂ = 0.05:0.05:5/98000 h ⁻¹	>90	250–400	—	[338]
10% WO ₃ /Ce _{0.68} Zr _{0.32} O ₂	NO/NH ₃ /O ₂ = 0.05:0.05:5/30000 h ⁻¹	>80	213–470	>97	[331]
10% WO ₃ /20%Ti-Ce _{0.68} Zr _{0.32} O ₂	NO/NH ₃ /O ₂ = 0.05:0.05:5/30000 h ⁻¹	>80	190–500	>99	[331]
15% WO ₃ /ZrO ₂ -Ce _{0.6} Zr _{0.4} O ₂	NO/NH ₃ /H ₂ O/O ₂ = 0.1:0.1:5:10/50000 h ⁻¹	>80	275–500	87	[334]
Ce _{1-x} Zr _x VO ₄ (x = 0.1–0.8)	NO/NH ₃ /O ₂ = 0.05:0.05:5/26000 h ⁻¹	>80	150–390	100	[333]
5% V ₂ O ₅ /Ce _{0.7} Zr _{0.3} O ₂	NO/NH ₃ /O ₂ = 0.1:0.1:5/70000 h ⁻¹	90	200	~100	[342]
FeW _{1.1} /Ce _{0.68} Zr _{0.32} O ₂	NO/NH ₃ /O ₂ = 0.1:0.1:5/30000 h ⁻¹	>90	245–455	~100	[337]
MnO _m /Ce _{0.5} Zr _{0.5} O ₂	NO/NH ₃ /H ₂ O/SO ₂ /O ₂ = 0.06:0.06:3:0.01:3/30000 h ⁻¹	>90	100–220	>85	[340]
MnO _m (0.4)/Co _{0.1} Ce _{0.45} Zr _{0.45} O ₂	NO/NH ₃ /H ₂ O/SO ₂ /O ₂ = 0.06:0.06:3:0.01:6/45000 h ⁻¹	>90	110–250	>85	[341]
15% Nb ₂ O ₅ /Ce _{0.75} Zr _{0.25} O ₂	NO/NH ₃ /H ₂ O/CO ₂ /O ₂ = 0.05:0.05:5:12:5/300000 h ⁻¹	>90	300–500	~100	[344]

X_{NO}, S_{N2} and T_r are denoted as NO_x conversion, N₂ selectivity, and reaction temperature range of NO complete conversion, respectively.

acid sites, which weakened the strong oxidation of NH₃ but enhanced the NH₃ adsorption capacity of catalyst. Therefore, the catalytic activity of the catalysts at high temperature was improved. Moreover, the introduction of sulfates to NiO/CZO led to high NH₃-SCR activity and N₂ selectivity. The addition of sulfates not only promoted the mobility of lattice oxygen by the formation of Niⁿ⁺-O-Sⁿ⁺ bond in CZO, but also inhibited NH₃ oxidation by reducing the amount of surface active oxygen [329].

Shen and Zhu *et al.* [330] studied the effect of fluorine additive on CeO₂-ZrO₂-TiO₂ (CZT) for NH₃-SCR. A series of CZT catalysts with different fluorine additives were synthesized by an impregnation method. The (001) facets were exposed on the catalyst surface with the modulation of HF. The grain size of TiO₂ increased and the specific surface area reduced after adding HF. However, the OSC of catalyst could be also enhanced with the modulation of HF. In addition, the synergy of (101) and (001) facets and the increase of surface chemisorbed oxygen and Ce³⁺ concentrations were beneficial to the improvement of catalytic activity. CZT-10F exhibited excellent catalytic performance for NH₃-SCR and more than 96% NO conversion at 360 °C under GHSV of 71400 h⁻¹.

Wang and Chen *et al.* [331,332] investigated the effect of titanium additive on a W/CZO monolithic catalyst for NH₃-SCR of NO_x. The doping of TiO₂ led to the formation of cerium-zirconium-titanium solid solution with large surface area. The interactions among metal oxides promoted the reductive behavior of the catalyst, which was helpful to enhance the NH₃-SCR activity at low temperature. Moreover, the addition of TiO₂ to CZO improved the adsorption and activation of NH₃ and increased the reactivity of adsorbed nitrate species with NH₃ species, and WO₃/CZT with 20% TiO₂ showed better deNO_x

activity and sulfur/water vapor tolerance than W/CZO.

Zhang and Huang *et al.* [333] developed a series of Ce_{1-x}Zr_xVO₄ solid solutions for NH₃-SCR of NO_x. The introduction of Zr into CeVO₄ considerably enhanced the specific surface area, redox property, active oxygen species as well as surface acidity of the catalysts, which were favorable for the improvement of SCR performance. The catalyst Ce_{0.85}Zr_{0.15}VO₄ exhibited the best low-temperature NH₃-SCR performance. T₅₀ was as low as 125 °C for above 80% NO conversion, and almost 100% N₂ selectivity was obtained in the range of 150–375 °C. Furthermore, the catalysts also showed excellent H₂O/SO₂ durability and good performance at high GHSV of 400000 h⁻¹.

4.3.1.2. Effect of active phase types

Kröcher *et al.* [334] prepared a 15% WO₃/ZrO₂-Ce_{0.6}Zr_{0.4}O₂ catalyst by the SC method. The catalyst showed more than 90% NO_x reduction efficiency between 300 and 500 °C, and it remained almost unchanged over the entire temperature range even after being aged at 700 °C. In addition, sulfur poisoning promoted the reduction efficiency of NO_x at high temperatures at the cost of a decreased low-temperature activity, but the catalyst could be fully recovered by heating in O₂ at 650 °C. Can *et al.* [335] investigated the catalytic performance of CZO-supported WO₃ catalysts for NH₃-SCR of NO_x. The addition of WO₃ on CZO induced a loss of the basic properties, the oxygen mobility, and the oxidation capacity of NO to NO₂, but it also led to a significant enhancement of NH₃ storage capacity, which seemed to play a significant role in NH₃-SCR reaction at high temperatures [336]. The changes in acid-base properties resulted in the enhancement of NH₃-SCR performance. All WO₃/CZO materials exhibited more than 80% NO_x reduction efficiency for NH₃-SCR at 350 °C in the presence of H₂O and CO₂

in feed gas. Xu and Chen *et al.* [337] reported that W/Fe ratio of $\text{FeW}_m/\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$ ($m = 0\text{--}1.38$) monolithic catalysts strongly affected the catalytic performance of the catalysts for $\text{NH}_3\text{-SCR}$ of NO_x . The $\text{FeW}_{1.03}/\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$ catalyst displayed the best catalytic performance, which exhibited 95% NO_x conversion and nearly 100% N_2 selectivity ranging from 250 to 435 °C. This should be due to the more chemically adsorbed oxygen species and Fe^{3+} active species as well as surface acid sites, which together contributed to the excellent catalytic activity of the $\text{FeW}_{1.03}/\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$ catalyst.

The effect of Mo addition on CZO catalysts for $\text{NH}_3\text{-SCR}$ of NO_x was studied by Liu and He *et al.* [338]. The addition of Mo inhibited the growth of CeO_2 particles, improved the redox ability, and increased the amount of surface acidity, especially the Lewis acidity. All of the characteristics were responsible for the excellent $\text{NH}_3\text{-SCR}$ performance. Among these, the $\text{CeMo}_{0.5}\text{Zr}_2\text{O}_x$ catalyst showed the best SCR activity, $\text{SO}_2/\text{H}_2\text{O}$ durability, and thermal stability. Interestingly, Liu and Li *et al.* [339] further confirmed the professional effect of Mo additive and proposed that the highly dispersed MoO_3 not only induced the formation of more Brønsted acid and Lewis acid sites on the catalyst surface, but also promoted the redox property of the catalyst. They should be accounted for the enhanced SCR activity.

A series of Mn/CZO catalysts with different Mn loading amounts were prepared to investigate the $\text{NH}_3\text{-SCR}$ performance of NO at low temperature. When Mn loading amounts increased, NO conversion on $\text{MnO}_m/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ first increased and then decreased. When $\text{Mn}/(\text{Ce} + \text{Zr}) = 0.6$, the activity reached the best. The E_a value of $\text{MnO}_m/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ catalyst was 18.1 kJ/mol, which was lower than that of $\text{MnO}_m/\text{TiO}_2$ (38 kJ/mol) [340]. Zhang and Shi *et al.* [155] combined the experiment and theory to investigate MnO_m/CZO nanorods for low-temperature $\text{NH}_3\text{-SCR}$ of NO. MnO_m on the surface of nanorods or $\text{Mn@CeO}_2(110)$ could easily produce a oxygen vacancy distortion. Moreover, the $\text{Mn@CeO}_2(110)$ model in the DFT analysis showed a prominent effect on NO and NH_3 adsorption, which resulted in a stronger nitrite intermediate (NOO^*) formation and more attractive interaction with NH_3 gas compared with those observed in the $\text{CeO}_2(110)$ model. A contrastive study on the difference between the introduction of cobalt in the active component and the support of Mn/CZO was made by Shen *et al.* [341]. Mn/Co-CZO exhibited a higher catalytic activity compared with Mn/CZO and Mn-Co/CZO because of the highly dispersed manganese oxides, good redox properties, more surface acid sites, and surface adsorbed oxygen species as well as more Mn^{4+} ion. Furthermore, Mn/Co-CZO also exhibited an outstanding SO_2 and H_2O -resistance.

Brückner *et al.* [342] investigated $\text{NH}_3\text{-SCR}$ of NO at low temperature over $\text{VO}_m/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0\text{--}1.0$) catalysts. 5% $\text{VO}_m/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts with $x = 0.7\text{--}0.9$ seemed to be promising catalysts, which exhibited almost 100% of both NO conversion and N_2 selectivity at 220 °C, and no deactivation took place during at least 190 h under a space velocity of 70000 h^{-1} . Reddy *et al.* [343] studied the effect of acidic and redox properties of a $\text{V}_2\text{O}_5/\text{CZO}$ catalyst in $\text{NH}_3\text{-SCR}$ of NO. SCR activity of $\text{V}_2\text{O}_5/\text{ZrO}_2$ was related to the support crystallinity, acidity, and

redox behavior. The $\text{V}_2\text{O}_5/\text{CZO}$ catalyst exhibited high activity and selectivity for $\text{NH}_3\text{-SCR}$ of NO and was less prone to unselective oxidation of NH_3 to N_2O . The effect of Nb loading amounts on the active sites and surface acidity of NbO_m/CZO for $\text{NH}_3\text{-SCR}$ of NO_x was studied by Wu *et al.* [344]. The catalyst with 15% Nb_2O_5 showed the best $\text{NH}_3\text{-SCR}$ activity and almost 100% N_2 selectivity in the temperature range of 190–460 °C at a high space velocity of 300000 h^{-1} . Altering the Nb loading amount would lead to the change in the structure and distribution of surface supported NbO_m species and evolution of electronic interaction between Nb species and CZO support. The electron transfer effect from Nb^{n+} to Ce^{m+} would result in the increase of Ce^{3+} , oxygen vacancies, and active oxygen. Moreover, the total surface acidity of the catalyst was remarkably enhanced after Nb loading, which could promote NH_3 adsorption and suppress the NH_3 unselective oxidation and be especially beneficial to SCR of NO_x at high temperatures (> 300 °C). Furthermore, the increased cerium sites with adjacent active oxygen contributed to the highly catalytic activity of the NbO_m/CZO catalyst at low temperatures. The effect of Nb introduction on the catalytic activity and hydrothermal stability of CZO catalyst for $\text{NH}_3\text{-SCR}$ of NO_x was reported by Liu and He *et al.* [345]. Nb additive to CZO not only increased the specific surface area and enhanced redox property, but also boosted the NH_3 adsorption and activation and promoted the reactivity of adsorbed nitrate together with NH_3 species. All of the above characteristics were responsible for the excellent $\text{NH}_3\text{-SCR}$ performance. The $\text{CeNb}_3\text{Zr}_2\text{O}_x$ catalyst exhibited superior SCR activity, high N_2 selectivity, and excellent hydrothermal durability, which still possessed high reductivity and abundant acid sites after being aged at 800 °C.

Si *et al.* [346] investigated the effect of zirconium phosphate addition to $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (ZP/CZO) on $\text{NH}_3\text{-SCR}$ of NO. The ZP/CZO catalyst showed superior catalytic activity and good N_2 selectivity at 250–450 °C under high space velocity of 300000 h^{-1} owing to the following two main factors. First, the zirconium phosphate provided adsorption sites for NH_3 on the catalyst surface, and the cerium sites acted as the redox sites for NO oxidation. The two distinct adsorption sites for NH_3 and NO_x resulted in a close contact between $\text{ads-NH}_3/\text{NH}_4^+$ and $\text{ads-NO}_3^-/\text{NO}_2^-$ species on the ZP/CZO catalyst (as illustrated in Fig. 20), which could rapidly react with NO together with active surface lattice oxygen. Second, the pre-combination of zirconium and phosphate could lower the interactions between phosphates and cerium ions. Thereby the mobility of surface lattice oxygen on the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst was maintained, which was beneficial to obtaining a catalyst with high $\text{NH}_3\text{-SCR}$ activity at low temperatures. Subsequently, the modification of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ by phosphate could enhance the hydrothermal stability and sulfur resistance of the catalyst [347].

4.3.1.3. Effect of preparation condition

Effect of calcination temperature on the structure and catalytic performance of the WO_3/CZO monolithic catalyst for $\text{NH}_3\text{-SCR}$ of NO_x was studied by Wang and Chen *et al.* [348]. SCR catalytic activity of WO_3/CZO was greatly enhanced by modestly rising the calcined temperature. WO_3/CZO calcination at

Fig. 20. Illustration of NH_3 -SCR reaction route on zirconium phosphate-CZO. Reprinted from [346] with permission.

500 °C exhibited the lowest light-off temperature of 173 °C and total conversion temperature of 205 °C, while WO_3/CZO calcination at 600 °C showed a broader temperature range (220–455 °C) with more than 90% NO_x conversion. The calcination temperature at 500 °C for WO_3/CZO was favorable for stabilizing the structure, increasing the amount of acid sites, Ce^{3+} , and surface active oxygen species, as well as enhancing reductivity of the catalyst. All of these together contributed to its better deNO_x activity at low temperatures. Zhang *et al.* [349] investigated the catalytic properties of $\text{CeO}_2\text{-ZrO}_2\text{-WO}_3$ (CZW) catalysts synthesized by various methods for NH_3 -SCR of NO_x . The CZW catalyst prepared by a hydrothermal method exhibited the optimal performance in the range of 175–450 °C due to the high specific surface area, the good redox behavior, the large amount of Ce^{3+} , and the chemisorbed oxygen species. Moreover, the highly dispersed WO_3 species over CZO and the abundant Brønsted acid sites were also responsible for the excellent SCR activity.

4.3.1.4. Mechanisms of NH_3 -SCR of NO_x over nanosize ceria-zirconium-based solid solutions

According to the studies of Gong *et al.* [350], Cai *et al.* [351], Brückner *et al.* [352], and Lee *et al.* [353], the mechanism of NH_3 -SCR of NO_x over CZO followed two distinct reaction pathways, the L-H mechanism at low temperature (< 200 °C) and the E-R mechanism at high temperature (> 200 °C):

In this SCR reaction, gaseous NH_3 molecules were first adsorbed on the Brønsted acid sites to generate NH_4^+ ions. Meanwhile, NO molecules were also adsorbed on the catalyst surface and were oxidized to NO_2 adspecies. Then one molecule

of NO_2 reacted with two adjacent NH_4^+ to generate active complex $\text{NO}_2(\text{NH}_4^+)_2$. $\text{NO}_2(\text{NH}_4^+)_2$ finally reacted with one molecule of NO to produce N_2 and H_2O and thus finished the catalytic cycle.

4.3.2. H_2 -SCR

Until the full transition to the hydrogen economy and zero emissions of greenhouse gases are realized, H_2 -SCR might be considered as a breakthrough NO_x control technology in favor of the current popular NH_3 -SCR. In 2014, Efstathiou *et al.* [354] for the first time reported the catalytic activity of W-promoted CZO (Ce-rich or Zr-rich) solids towards H_2 -SCR of NO_x . In the range of 250–350 °C and at GHSV = 51000 h^{-1} , NO_x conversions were in the 30%–55% range with 85%–92% N_2 selectivity (Fig. 21). A good stability of both Zr-rich and Ce-rich W/CZO catalysts was also obtained at 300 or 250 °C even after 66 h on-line reaction. The introduction of about 7 vol% H_2O in the feed stream resulted in a 10%–15% drop in NO_x conversions in the range of 250–300 °C, but an improvement in N_2 selectivity by about 5%. Moreover, the specific integral reaction rate of Zr-rich W/CZO towards H_2 -SCR in the range of 250–350 °C was as 2–3 times as that on Ce-rich W/CZO solid. Recently, Li *et al.* [355] prepared a Pd catalyst with highly dispersed Pd nanoclusters on an Al-doped CZO mixed oxide for low-temperature H_2 -SCR of NO_x with excess O_2 . The introduction of Al into CZO could effectively reduce the crystallite size and enhance the specific surface as well as increase the surficial Ce^{3+} concentrations and adsorbed oxygen species. As a result, a remarkable hydrogen spillover ability was achieved. The supported Pd nanoclusters showed 84% NO_x conversion in the temperature range of 100–300 °C.

Liotta *et al.* [356] investigated the effect of the strong metal-support interaction (SMSI) on the catalytic activity of a $\text{Pt}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst for H_2 -SCR of NO_x . The catalytic activity was enhanced for the catalyst pre-treated in H_2 at 350 °C compared with the samples performed at 800 and 1050 °C. Moreover, transient reactivity tests of NO reduction by H_2 were also conducted. As expected, the sample pre-reduced at 350 °C showed higher activity. The pretreatments had no effect on the N_2 selectivity at the temperature of the maximum NO_x conversion. Therefore, it demonstrated the presence of SMSI effect between Pt and ceria and the important role of Pt in promoting the CZO structural reorganization. Such type of interaction determined a decrease of Pt and ceria reduction temperature and a stabilization of Pt oxide even in reducing atmosphere at high temperature. Efstathiou *et al.* [357] reported a series of $\text{Pt}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0.4\text{--}0.6$) solids to be used for the SCR of NO under lean burn conditions (2.5% O_2) using C_3H_6 and H_2 as reducing agents. These $\text{Pt}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts showed significant differences for H_2 -SCR performance in the range of 120–180 °C but practically exhibited the same catalytic behavior at higher temperatures. It was proved that the active NO_x of H_2 -SCR path resided within a reactive zone around each Pt nanoparticle, which extended to less than one lattice constant on the support surface. In addition, a remarkable activity and N_2 selectivity enhancement was observed at temperature above 400 °C when both H_2 and C_3H_6 reducing agents were used

Fig. 21. (a) NO_x conversion (X_{NO_x} , %), H_2 conversion (X_{H_2} , %), (b) N_2 selectivity (S_{N_2}) and N_2O formation (ppm) in H_2 -SCR as a function of temperature over W-CeZr catalysts. Reaction conditions: 520 ppm NO_x ($\text{NO}:\text{NO}_2 = 9:1$), 1.0% H_2 , 5% O_2 , 10% CO_2 and He as balance gas, GHSV = 51000 h^{-1} . Reprinted from [354] with permission.

compared to H_2 -SCR or C_3H_6 -SCR alone. This synergy effect was explained to arise mainly because of the increase of θ_{H} in the presence of $-\text{CH}_x$ species derived from adsorbed C_3H_6 decomposition on Pt, which blocked sites of oxygen chemisorption. The increase of surface oxygen vacancies promoted the formation of a more reactive chelating nitrite (NO_2^-) species compared to the case of H_2 -SCR.

4.3.3. HC-SCR

Although SCR of NO_x by NH_3 or urea has proven to be an effective method for reducing NO_x emissions, there are several problems inevitably existing in the present NH_3 -SCR technology, such as NH_3 slip, air-heaters fouling storage hazards, ash odor, equipment corrosion, and high running cost. Thus, a very significant market potential exists for an improved technology in this area. As a result, SCR of NO by HC derived from on-board fuel has attracted a lot of attention in the past years [320,358–361], as displayed in Table 7.

4.3.3.1. CH_4 -SCR

As the main component of natural gas, CH_4 is an attractive reductant of NO_x for a number of power sources. Nevertheless,

the chemical stability of CH_4 implies high activation temperature and, usually, a poor selectivity towards the reduction of NO by CH_4 is obtained. Therefore, only a limited number of noble metals can act as the active component, such as Pd [355,362–365]. In 2004, Granger *et al.* [366] explored CH_4 as alternative in SCR of NO in the presence of oxygen over Pd/CZO under lean conditions. The activation procedure under O_2 or H_2 drastically influenced the catalytic performance of the catalyst. Pd/ $\text{Ce}_{0.52}\text{Zr}_{0.48}\text{O}_2$ showed a higher activity and a better N_2 selectivity under O_2 than that under H_2 , indicating that oxygen could enhance the activity. Moreover, the stabilization of a metallic or oxidic Pd phase led to poor activity in the conversion of NO in the absence of oxygen. Azambre *et al.* [367] reported Pd supported on sulfated CZO catalysts for CH_4 -SCR of NO_x and investigated the correlation between catalytic performance and nature of active Pd species. The catalytic activity was mainly dependent on the Pd loading amount. At low Pd loadings, Brönsted acidity of the sulfated support was beneficial to stabilizing Pd to form highly dispersed Pd species, which existed as $[(\text{PdO})_m\text{-H}]^{n+}$ adducts located in the vicinity of sulfate species. The corresponding 0.24%–0.53% Pd/sulfated-CZO catalysts exhibited 30%–35% NO_x conversion to N_2 around 370 °C. By

Table 7

Catalytic activity of nanosize CZO materials in HC-SCR of NO_x .

Catalyst	Reaction conditions	X_{NO} (%)	T_r (°C)	S_{N_2} (%)	Ref.
$\text{Ce}_{0.7}\text{Zr}_{0.3}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2 = 0.0247:0.025:5/30000 \text{ h}^{-1}$	9–27	180–430	—	[373]
3%W-CZO	$\text{NO}/\text{NO}_2/\text{H}_2/\text{O}_2/\text{CO}_2/\text{H}_2\text{O} = 0.0468:0.0052:1/5/10/7/51000 \text{ h}^{-1}$	56	300	77–92	[354]
1% Ni/Al-Ce _x Zr _{1-x} O ₂	$\text{NO}/\text{NO}_2/\text{H}_2/\text{O}_2 = 0.09:0.01:1:5/60000 \text{ h}^{-1}$	10–12	100–300	—	[355]
4% Cu-1% Ag/ $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2 = 0.2:0.2:10/30000 \text{ h}^{-1}$	56–89	335–550	—	[372]
0.1% Pt/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	$\text{NO}/\text{H}_2/\text{O}_2 = 0.015:0.8:2.5/33000 \text{ h}^{-1}$	60–92	170–300	70–82	[357]
0.1% Pt/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2 = 0.015:0.5:2.5/33000 \text{ h}^{-1}$	50	350	78	[357]
0.1% Pt/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	$\text{NO}/\text{H}_2/\text{HC}/\text{O}_2 = 0.015:0.8:0.5:2.5/33000 \text{ h}^{-1}$	100	450–600	95–98	[357]
1% Pt/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2 = 1:3:3/40000 \text{ h}^{-1}$	80	500	—	[375]
1% Pt/ $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2 = 0.1:0.1:5/60000 \text{ h}^{-1}$	60	250	74	[356]
1% Pd/Al-Ce _x Zr _{1-x} O ₂	$\text{NO}/\text{NO}_2/\text{H}_2/\text{O}_2 = 0.09:0.01:1:5/60000 \text{ h}^{-1}$	>84	100–300	—	[355]
0.89% Pd/ $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2 = 0.034:0.19:8/112500 \text{ h}^{-1}$	29	243	87	[369]
1% Pd/ $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$	$\text{NO}_2/\text{CH}_4 = 1:1/4200 \text{ h}^{-1}$	100	495–700	100	[368]
Sulfated 1% Pd/ $\text{Ce}_{0.52}\text{Zr}_{0.48}\text{O}_2$	$\text{NO}/\text{CH}_4/\text{O}_2 = 0.015:0.15:7/40000 \text{ h}^{-1}$	5–15	250–500	—	[367]
0.52% Rh/ $\text{Ce}_{0.62}\text{Zr}_{0.38}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2 = 0.0247:0.025:5/30000 \text{ h}^{-1}$	52	360	—	[374]
0.4% Rh/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2/\text{H}_2\text{O} = 0.05:0.1167:0.5/500000 \text{ h}^{-1}$	100	400–600	—	[370]
0.44% Rh-0.54%Pd/ $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2 = 0.034:0.19:8/112500 \text{ h}^{-1}$	28	288	81	[371]
0.44% Rh-0.91%Pt/ $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$	$\text{NO}/\text{HC}/\text{O}_2 = 0.034:0.19:8/112500 \text{ h}^{-1}$	16	289	85	[371]

X_{NO_x} , S_{N_2} and T_r denote NO_x conversion, N_2 selectivity, and reaction temperature range of NO complete conversion, respectively.

contrast, higher Pd loading amounts were detrimental for the SCR reaction due to the promoted formation of PdO_m clusters, which showed more active in the selective oxidation of CH_4 . In addition, the introduction of H_2O to the feed was unfavorable due to the prevention of NO_x and CH_4 sorption at low-medium temperatures. The reaction intermediates involved in CH_4 -SCR and the factors controlling the reactivity of Pd/CZO catalyst were studied by Azambre *et al.* [368]. By DRIFTS of adsorbed CO, it was found that Pd species on $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ were mainly present in Pd^{x+} ionic form surrounded by surface oxygens or small PdO_m clusters cationic form. The investigation of temperature-programmed surface reaction in $\text{CH}_4 + \text{NO}_2$ atmosphere indicated that CH_4 -SCR reaction on Pd/ $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ was initiated at 280 °C and yielded almost 100% N_2 above 500 °C. DRIFTS-MS and TGA experiments showed that deNO_x activity was due to a surface reaction between adsorbed CO_x species, which were generated by CH_4 activation on reduced Pd sites with $\text{ad-N}_x\text{O}_y$ species presumably located on the support. The detrimental effect of O_2 on deNO_x was due to the promotion of the complete combustion of CH_4 assisted by the ceria-zirconia component at the expense of SCR reaction above 320 °C.

4.3.3.2. C_3H_6 -SCR

Compared to H_2 , CH_4 , much more efforts have been made to improve NO removal using C_3H_6 as reductant. Thomas *et al.* [369] investigated C_3H_6 -SCR of NO_x on Pd/ $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$ catalysts (Pd/CZO). The addition of Pd to CZO significantly promoted the reduction of NO by C_3H_6 , and the catalyst still exhibited relative high deNO_x activity even in the presence of 1.7% H_2O . Pd/CZO displayed much higher N_2 selectivity than Pd^0/SiO_2 , indicating that the lean deNO_x mechanism occurring on these catalysts should be different from that of Pd^0/SiO_2 .

Haneda *et al.* [370] studied the catalytic performance of Rh supported on CZO for C_3H_6 -SCR of NO. The catalytic activity of Rh/CZO strongly depended on the Ce/Zr ratio. Rh/ $\text{Ce}_{0.50}\text{Zr}_{0.50}\text{O}_2$ showed the best activity. Moreover, the activity of Rh/CZO for C_3H_6 -SCR of NO also depended on the reaction gas conditions. The presence of O_2 could inhibit NO reduction by C_3H_6 , especially for Rh/ $\text{Ce}_{0.74}\text{Zr}_{0.26}\text{O}_2$. The effect of the nature of platinum group metals (PGMs: Pd, Rh, Pt) on the lean C_3H_6 -assisted removal of NO on $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$ -supported catalysts was investigated by Thomas *et al.* [371]. The order of reactivity of CZO-supported PGMs was $\text{Pd} \geq \text{Pt} \geq \text{Rh}$, and CZO-supported catalysts exhibited higher N_2 selectivity than those supported on SiO_2 or Al_2O_3 . The higher catalytic activity of Pd-based catalysts for C_3H_6 -SCR of NO_x might be associated with the greater ability of the PdO_x phase to adsorb NO_2 .

Amin *et al.* [372] studied the catalytic activity of CZO-supported Cu and Ag for C_3H_6 -SCR of NO. Compared to $\text{Cu}(4)/\text{Ag}(1)/\text{CeO}_2$, $\text{Cu}(4)/\text{Ag}(1)/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ displayed higher deNO_x activity in the range of 250–350 °C. The SMSI and high redox property of the support exhibited by the $\text{Cu}(4)/\text{Ag}(1)/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst were considered to be the main reasons of the improvement of C_3H_6 -SCR performance. In addition, reaction temperature was found to affect NO reduction activity more significantly than NO and C_3H_6 concentrations. The optimum conditions were estimated to be 415.4 °C,

1827.2 ppm of NO, and 1908.1 ppm of C_3H_6 concentration corresponding to NO conversion of 82.9%.

4.3.3.3. Other C_xH_y -SCR

Compared with CH_4 -SCR and C_3H_6 -SCR, more research has been performed on SCR of NO_x with a mixture of HC representative of the exhaust gas from fossil fuel combustion (C_3H_8 , C_3H_6 , and C_7H_8) over CZO catalysts. Costa *et al.* [373] studied the relationship between the surface properties and deNO_x activity of CZO. $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x = 0.17\text{--}0.8$) were active in deNO_x reaction, and their catalytic activities varied with the different cerium amounts and reached the maximum for $x = 0.62$ with 27% NO_x transformation to N_2 at 322 °C. Subsequently, Costa *et al.* [374] investigated CZO-supported rhodium catalyst for NO_x reduction, and the catalytic activities were evaluated by isothermal steady-state experiments using a mixture of exhaust gases of HC. The addition of Rh on $\text{Ce}_{0.62}\text{Zr}_{0.38}\text{O}_2$ considerably improved the catalytic activity during the deNO_x process assisted by HC, and decreased by about 34 °C for the temperature of NO_x conversion to N_2 , which went up to 57%. The effect of support on the three-way catalytic HC- NO - O_2 reaction over Pt/CZO catalysts under reducing conditions was investigated by means of operando X-ray absorption near edge structure [375]. The formation of active metallic Pt sites and the self-poisoning effect of adsorbed carbonaceous species on metallic Pt should determine the start-up behavior of catalytic reaction over supported Pt catalysts. The oxygen reactivity in the support oxide was also important for reducing the catalytic start-up temperature in addition to the suitable Pt reduction temperature.

4.3.3.4. Mechanisms of HC-SCR of NO_x over nanosize ceria-zirconium-based solid solutions

The reduction mechanism of NO_x by HC over CZO is very complex [376–381]. According to the mechanism proposed by Djéga-Mariadassou *et al.* [379] (as shown in Fig. 22), the first step of this catalyst is to oxidize NO to NO_2 . The second step is the mild oxidation of HC by NO_2 to form oxygenate species, which plays an important role in the catalyst regeneration process. The release of N_2 occurs in step 3. It involved NO_x dissociation and followed by the formation of N_2 and scavenging of the adsorbed oxygen species left from NO dissociation. The removal of the adsorbed oxygen was due to the total oxidation of an activated reductant ($\text{C}_x\text{H}_y\text{O}_z$). In addition, both steps 2 and 3 have to turn over simultaneously. However, at the molecular level, the both steps were not in the same catalytic cycle.

Fig. 22. Catalysis-assisted deNO_x reaction: each cycle corresponds to one function (F1, F2, and F3).

4.3.4. $C_xH_{2x+1}OH$ -SCR

For deNO_x reaction, it has been reported that when a hydrocarbon is able to catalytically reduce NO_x, its corresponding alcohol must also be useful for such a process [382]. The role of CH₃OH in the reduction of NO_x to N₂ was investigated over H₃PW₁₂O₄₀-Pt/CZO [383]. The reduction of NO_x went through two stages. First, during the lean mode for 2 min, NO_x (NO/NO₂ = 1) were stored in the catalyst; second, they were reduced into N₂ during the rich period (CH₃OH injection 1 min). With CH₃OH, NO_x storage efficiency of H₃PW₁₂O₄₀-Pt/CZO was stable and high (ca. 100%), and about 55% of stored NO_x were reduced into N₂ by alternative lean/rich cycles. $C_xH_yO_z$ intermediate species derived from methanol were thought to be the intermediate reductants for NO_x.

Azambre *et al.* [384] studied the catalytic performance of sulfated CZO catalysts for SCR of NO_x by ethanol. The sulfated CZO catalysts were prepared by direct sulfation of the crystallized CZO nanopowders with 0.5 mol/L H₂SO₄. The sulfation treatment enhanced the SCR activity via the promotion of alternative pathways for the formation of N₂ and the prevention of combustion reactions at medium temperatures. Moreover, NO_x conversion was shown to exceed 30% on most of SCR catalysts in the range of 250–400 °C. Above 350–400 °C, the N₂ selectivity was close to 100% and an optimum deNO_x yield of 48% was achieved for a sulfated catalyst with a Ce molar fraction of 0.5. Azambre and his coworkers [385] further studied the effect of Ag, Pd and Co additive on the SCR of NO_x by ethanol over sulfated CZO catalysts. The metal promoters have a discrete effect on C₂H₅OH-SCR activity, often negative and sometimes positive. Positive effects essentially arised from the formation of acetaldehyde, which was the most effective reductant of the system. It occurred mostly in the presence of Ag species in the +1 oxidation state. By contrast, the Pd catalyst was not effective for C₂H₅OH-SCR because it induced a depletion of the organics needed for NO_x reduction by promoting total oxidation reactions. Another negative effect was the inhibition of the most active cerium sites of the support, which led to a decrease of the SCR activity at low temperatures and the shift of deNO_x window towards the high temperatures.

Djéga-Mariadassou *et al.* [386] investigated the catalytic performance of 1-propanol-assisted reduction of NO_x over a Ir/Ce_{0.6}Zr_{0.4}O₂ catalyst. This catalytic material showed a promotional effect of iridium on the conversion of NO_x. Ir/Ce_{0.6}Zr_{0.4}O₂ exhibited a higher NO_x reduction (25% at 225 °C) than Ce_{0.6}Zr_{0.4}O₂ (19% at 260 °C). 1-Propanol was activated at lower temperatures over the Ir catalyst. Moreover, R-NO_x species were found to be the intermediates of the deNO_x process, which provided the partially oxidized species required by the deNO_x model.

4.4. Nanosize ceria-zirconium-based solid solutions for NO_x direct decomposition

4.4.1. NO direct decomposition

Although several methods exist to eliminate NO, direct decomposition of NO to N₂ and O₂ ($NO \rightarrow 1/2N_2 + 1/2O_2$) is recognized to be one of the most attractive methods because it

does not need any reductants and is simple and economical. NO is thermodynamically unstable. However, it does not decompose easily due to its high *E_a* value (364 kJ/mol). Therefore, a proper catalyst is needed to lower *E_a* value in order to facilitate the decomposition. Research in this domain has been extensively performed on noble metal-supported catalysts [387,388], metal oxides [389–394], carbon [395–397], and zeolite-based catalysts [398–404]. Whereas, little research was reported on the direct decomposition of NO_x over CZO-based catalysts. Cheng *et al.* [405] prepared nanosize CZO-supported H₃PW₁₂O₄₀ (HPW) for NO capture and decomposition. CZO exhibited remarkable promotion effect on the capture of NO_x. For HPW/CZO prepared by a mechanical grinding method, NO_x adsorption efficiency was considerably enhanced with increasing HPW loading amounts in the range of 20%–70%. However, the deNO_x efficiency decreased with increasing loading of HPW (> 70%). Subsequent to the adsorption process, the adsorbed NO_x decomposed to N₂ upon heating from 150 to 450 °C, with a N₂ yield of 27.3%. Yang *et al.* [406] reported a Ce-Cu-Zr/ZSM-5 catalyst prepared by an ion-exchange method showing high catalytic activity for NO decomposition in the presence of O₂, and the highest NO conversion was up to 75%. This indicated that the introduction of CZO could promote the formation of a new highly active site, which facilitated oxygen mobilization and desorption, thereby enhanced the activity of catalysts.

4.4.2. N₂O direct decomposition

Besides NO, nitrous oxide (N₂O) has drawn ever increasing attention in the past decades because of its detrimental green house effect and ozone-depleting action [322,407–410]. Thus, the development of highly active catalysts to purify N₂O is becoming an important issue. Imamura *et al.* [411] investigated the effects of structural composition and calcination temperature of the catalysts on the catalytic performance of Rh/CZO for N₂O decomposition. The incorporation of Zr into ceria significantly enhanced its thermal stability to retain high specific surface area even at the calcination temperature of 900 °C. Rh/Ce_{0.7}Zr_{0.3}O₂ exhibited the optimal catalytic activity due to the highly dispersed Rh species exposed to the support surface. Nevertheless, too high calcination temperature (1200 °C) led to the remarkable decrease of catalyst surface area and the aggregation of Rh.

So far, NO_x direct decomposition over metal surfaces, oxides, or zeolites is faced to some serious practical difficulties. NO_x decomposition process is a high-temperature reaction, which is undesirable. NO_x dissociation over single crystal metal easily reoxidizes the metal surface, which in turn hinders the NO_x dissociation process. So, a reducing agent is needed to scavenge the dissociated oxygen. From an exhaust catalysis view, it is not sufficient to dissociate NO_x, and other pollutants like CO and HC should also be oxidized. Therefore, NO_x reduction by H₂, HC, and NH₃ is more attractive for NO_x abatement.

4.4.3. Mechanisms of NO_x direct decomposition over nanosize ceria-zirconium-based solid solutions

It is widely accepted that N₂O decomposition is a sensitive reaction to oxygen mobility.

In this mechanism, the asterisk (*) is a coordinatively unsaturated site of oxidic transition for N_2O adsorption. The first step for N_2O decomposition was the adsorption of N_2O followed by its decomposition, leading to N_2 formation in association with surface oxygen. In this classical model, oxygen formation occurred through recombination of two adsorbed atomic oxygen species (O^*) or through reaction of N_2O with adsorbed atomic oxygen species.

4.5. Nanosize cerium-zirconium-based solid solutions for simultaneous removal of CO and NO_x

The simultaneous removal of CO and NO_x in the presence or absence of O_2 , CO_2 , and H_2O is a proper model reaction, which is different from real automobile exhaust emission. However, the fundamental studies using the supported noble and non-noble metal catalysts were performed to get more insight into the nature of this reaction [412–416], as shown in Table 8.

4.5.1. Pt-based ceria-zirconium catalysts

Rao *et al.* [417] reported CZO-supported Rh catalysts for NO + CO reaction. The activation of the reductant was difficult on the bare support, and the presence of Rh was necessary to activate and spill it over to the support. Moreover, the bulk oxygen vacancy played an important role in promoting NO conversion over Rh/CZO catalysts, and oxygen vacancy gradient was indicated as the main driving force for NO dissociation. Ihm *et al.* [418] investigated the catalytic activities of Pt/ WO_3 /CZO catalysts for NO + CO reaction with or without oxygen. Pt/ CeO_2 and Pt/CZO could be readily reduced by CO, while the reduction was significantly inhibited with the introduction of WO_3 for Pt/ WO_3 /CZO. It was due to that WO_3 addition suppressed the formation of the active sites for NO reduction. Pt/ WO_3 / ZrO_2 showed a slightly higher activity than Pt/ ZrO_2 . As reported by Regalbuto and Wolf [419], Pt- WO_3 adlineation sites exhibited very high NO dissociation activity and increased the activity

toward NO + CO reaction. However, based on the results displayed in Fig. 23, there was no obvious correlation between acidity and catalytic activity for NO + CO reaction over Pt/ WO_3 / CeO_2 / ZrO_2 catalysts in the absence of oxygen. With excess oxygen, Pt/ WO_3 /CZO and Pt/ WO_3 / ZrO_2 catalysts showed higher NO conversion to N_2 and N_2O particularly at low temperature. This was attributed to the enhanced acidity from ZrO_2 and WO_3 in the Pt/ WO_3 / CeO_2 / ZrO_2 catalysts in the presence of excess oxygen.

4.5.2. Pd-based ceria-zirconium catalysts

Wang *et al.* [420] prepared a series of mesoporous $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ solid solutions with cationic defects by a surfactant-controlled synthesis method, and the pore size of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ could be governed by the incorporation of the surfactant into solid network and the calcination temperature. In the cold start of reaction, NO reduction by CO with excess oxygen over the 3% Pd/ $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst presented 100% selectivity to N_2 . At reaction temperatures below 200 °C, NO restrained the oxidation of CO. However, above 200 °C, CO oxidation showed an inhibition effect on NO conversion, and there was a reaction competition between NO reduction by CO and CO oxidation by O_2 . The key factor of the reaction competition was the concentration of CO and O_2 . The different oxygen concentration also influenced Pd state. High coverage of Pd surface by oxygen was favorable for NO oxidation to NO_2 but suppressed NO decomposition to N^* and O^* . Fernández-García *et al.* [421] investigated the light-off behavior for CO + NO reaction over Pd/CZO/ Al_2O_3 catalysts prepared by the ME method. The promoting effect of CZO was present in both CO oxidation and NO reduction reactions, and it was dependent on the characteristics of the promoter and the nature of the reaction. CO oxidation activity was greatly enhanced by contact between Pd and the 3-D aggregated promoter, and the catalytic activity increased with increasing CZO content. Fernández-García and co-workers [422] further studied the catalytic activity of a series of Pd-Cr bimetallic catalysts supported on a CZO/ Al_2O_3 mixed support for CO + NO + O_2 reaction. The catalytic activities of these bimetallic catalysts were strongly influenced by the nature of the support. For the Al_2O_3 support, an interaction

Table 8

Catalytic Activity of nanosize CZO materials in simultaneous removal of CO and NO_x .

Catalyst	Reaction conditions	<i>T</i> (°C)	X_{NO} (%)	X_{CO} (%)	Ref.
1.23CuO/ $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$	0.05 g/NO:CO/He = 1:2:17/12000 h ⁻¹	400	100	—	[416]
4% Cu/ $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$	0.1 g/NO:CO/He = 0.3:0.3:99.4/50000 h ⁻¹	400	100	92~96	[425]
0.4CuO/ $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ /γ- Al_2O_3	0.05 g/NO:CO/He = 1:2:17/12000 h ⁻¹	400	100	—	[426]
yCuO/ $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ (y = 0.3, 0.6, 0.9, 1.2, 1.5)	0.05 g/NO:CO/He = 1:2:17/12000 h ⁻¹	400	100	—	[429]
yCo-0.5Cu/ $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$ (y = 0.08, 0.16, 0.32)	0.05 g/NO:CO/He = 1:2:17/24000 h ⁻¹	400	100 (y = 0.08)	90	[428]
0.08Mn-0.5Cu/ $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$	0.05 g/NO:CO/He = 1:2:17/24000 h ⁻¹	400	100	90	[429]
0.5% M/ $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ (M = Rh, Pt)	0.04-0.008 g/NO:CO/He = 1:3:96/12000–50000 h ⁻¹	400	100 (M = Pt)	—	[417]
1% Pt/15% WO_3 - $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$	0.5 g/NO:CO/He = 0.5:0.5:99/40000 h ⁻¹	400	90	73	[418]
y% Rh/ $\text{Ce}_{0.65}\text{Zr}_{0.35}\text{O}_2$ (y = 0.05~1)	0.5 g/NO:CO/ O_2 /He = 0.1:1:0.45:98.45/40000 h ⁻¹	400	100	100	[424]
1% Pd/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	3.4 g/NO:CO/ O_2 /He = 1:1:0.45:97.55/30000 h ⁻¹	400	18	100	[421]
3% Pd/ $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	0.05 g/NO:CO/ O_2 /He = 0.023:0.0685:1:98.908/70000 h ⁻¹	400	70	100	[420]
1% PdNi/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	NO:CO/ O_2 /He = 0.1:1:0.45:98.45/30000 h ⁻¹	400	30	100	[423]
1% PdCr/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ / Al_2O_3	3.4 g/NO:CO/ O_2 /He = 0.1:1:0.45:98.45/30000 h ⁻¹	400	6	68	[422]

X_{NO} , X_{CO} and *T* are denoted as NO_x conversion, CO conversion and reaction temperature, respectively.

Fig. 23. Catalytic activities for the removal of NO + CO over various catalysts (CO: 0.5%, NO: 0.5%). Reprinted from [419] with permission.

between Pd and Cr existed in the calcination state, and the mixed oxide phase containing Pd⁺ and Cr³⁺ appeared to be the main factor leading to the enhancement in CO oxidation and the decrease in NO reduction compared with the monometallic system. In the case of the CZO/Al₂O₃ mixed support, the introduction of Cr was less influential for catalytic activity. The effect of Ni on the catalytic activity of Pd-Ni/CZO/Al₂O₃ catalysts for stoichiometric CO and NO elimination was investigated by Martínez-Arias *et al.* [423]. A significant dependence on the support nature in terms of catalytic changes was produced by Ni. The introduction of Ni considerably promoted the CO oxidation activity over the CZO/Al₂O₃-supported catalyst. This was due to the changes of Pd distribution over the support, which favored the formation of active Pd-CZO interfaces. The significant extent of such a promoting effect revealed an important role of the particle size of CZO component on such catalytic processes.

4.5.3. Rh-based ceria-zirconium catalysts

Compared with Pt- and Pd-based CZO catalysts, Rh-based CZO catalysts get relatively less attention. In 2009, Ihm *et al.* [424] prepared CZO by supercritical synthesis and CP methods as support for a Rh catalyst. The catalytic activities of the catalysts were investigated for NO + CO reaction. Rh/CZO prepared by a supercritical synthesis method exhibited better reducibility and higher thermal stability as well as better performance for the catalytic reduction of NO by CO than that prepared by a CP method. CZO prepared by the supercritical synthesis method showed more potential applications as catalyst support due to its sparsely-agglomerated morphology and higher thermal stability.

4.5.4. Cu-based ceria-zirconium catalysts

In addition to CZO-supported noble metals (Pt, Pd, Rh) catalysts, considerable efforts have been devoted to developing promising Cu-based catalysts for NO + CO reaction. Zhang *et al.* [425] investigated the catalytic activity of 4% Cu/Ce_xZr_{1-x}O₂ ($x = 0-1.0$) catalysts for the reduction of NO by CO. The incorporation of Zr⁴⁺ into CeO₂ could stabilize Cu⁺ species, which was favorable for the initial reductive chemisorption of NO to N₂O. Cu/Ce_{0.75}Zr_{0.25}O₂ showed an excellent low temperature activity

with 40% N₂ yield at 150 °C due to its abundant surface reactive oxygen sites and high reducibility, and N₂ yield > 85% was obtained for all Zr-containing catalysts at 250 °C and above. Gao *et al.* [426] studied the effects of Ce/Zr molar ratios on the physicochemical properties of CuO/Ce_xZr_{1-x}O₂/γ-Al₂O₃ catalysts for NO + CO reaction. The ceria-rich catalyst showed higher activity and TOF value towards NO reduction compared with the pure ceria and zirconia-rich ones due to the difference in the interaction among Cu, Ce_xZr_{1-x}O₂, and γ-Al₂O₃ support. Dong *et al.* [427] prepared a series of CuO/Ce_xZr_{1-x}O₂ catalysts with different Cu loading amounts and Ce/Zr molar ratios and studied the correlation of structural characteristics with catalytic performance for NO reduction by CO. The ceria-rich (pseudo-cubic *t'*) phase could disperse and stabilize the copper species more effectively and resulted in stronger interaction with copper than the zirconia-rich (*t*) phase. Furthermore, compared with the zirconia-rich phase, the synergistic interaction of Cu with ceria-rich phase easily promoted the reduction of copper species and surface oxygen as well as the activation of adsorbed NO species. Therefore, the CuO/Ce_{0.8}Zr_{0.2}O₂ catalyst exhibited the higher activity for NO reduction than CuO/Ce_{0.5}Zr_{0.5}O₂ and the CuO/Ce_{0.2}Zr_{0.8}O₂ catalysts.

Compared with CZO-supported mono-metal catalysts, binary metal oxides possess more active species, which may be more favorable for the catalytic reaction of NO + CO. Dong and co-workers [428] investigated the activity of binary metal oxides Ce_{0.67}Zr_{0.33}O₂ supported CuO-CoO_m catalysts for the removal of NO and CO. The addition of cobalt species significantly improved the activity of NO + CO by promoting the reduction of dispersed copper oxide. FT-IR results further revealed that the addition of cobalt oxide changed the adsorption type of NO and CO on the catalysts, and oxidized NO dimers into ionic NO₃⁻, and then these partial surface active species might be reduced into low-valence state above 300 °C. Subsequently, they investigated the effect of MnO_m modification on the activity of the CuO/Ce_{0.67}Zr_{0.33}O₂ catalyst for NO reduction by CO [429]. The introduction of Cu and Mn species induced the expansion of lattice and the decrease of microstrain of CZO, thereby promoting the formation of oxygen vacancies. The addition of Mn species could promote the reduction of the catalysts and assist

copper oxide in changing the valence and supplying oxygen. These reduction behavior was dependent on the loading amounts of MnO_m and the impregnation procedure. In addition, the introduction of MnO_m could not change the adsorption type of NO, but readily facilitated the activation of the adsorbed NO species. As a result, these factors were responsible for the enhancement of activity and selectivity through MnO_m modification.

4.5.5. Mechanisms of simultaneous removal CO and NO reaction over nanosize ceria-zirconium-based solid solutions

There are two mechanisms related to simultaneous removal CO and NO, the redox mechanism and the organonitrogen mechanism. The redox mechanism involves an initial dissociation-chemisorption of NO, which forms a N_2O intermediate and an oxidized surface, and then CO further reduces N_2O into N_2 and restores the original catalytic surface [237,430]. By contrast, the organonitrogen mechanism includes the generation of isocyanate compounds as an intermediate [431,432]. In the catalytic reduction of NO_x , the two reaction mechanisms may occur simultaneously, and the contribution of each mechanism may depend on the reductant type, catalyst nature, and reaction conditions (temperature, space velocity, concentration, etc.) [433,434]. Zhang and Kaliaguine *et al.* [430] proposed that CO + NO reaction mechanism on Cu/CZO involved the dissociation and reduction of chemisorbed NO_x .

At the 50–250 °C low-temperature region:

At the high-temperature range above 250 °C:

Oxidation of intermediate carbonaceous species:

Sun and Dong *et al.* [428] reported a possible reaction mechanism over CuCo/CZO catalysts for NO + CO reaction:

NO was assumed to preferentially adsorb over dispersed copper oxide or oxygen vacancy sites of CZO to form chelating nitrite and $\text{cis-N}_2\text{O}_2^{2-}$ below 300 °C (Eqs. (49) and (50)). These adsorbed NO_x species reacted with CO activated by Cu^+ species,

and then N_2O and CO_2 were produced. When the temperature was over 300 °C, the catalyst could be reduced by CO to Cu^+ and Co^{2+} ions. The catalytic reduction of NO to N_2 was generated by CO. The main Cu^+ species contributed to N_2O reduction by CO, while the dispersed cobalt oxides played an important role in N_2O decomposition and reduction by CO, as shown in Eqs. (51) and (52).

4.6. Nanosize cerium-zirconium-based solid solutions for simultaneous removal of NO_x and soot

The simultaneous removal of NO_x and soot using one catalytic material was proposed for the first time by Yoshida *et al.* [435], which seems to be one of the most effective and economic after-treatment techniques. The key challenge is to find a catalyst that can achieve a high rate of soot oxidation in combination with substantial NO_x reduction at sufficiently low temperature. Several kinds of catalysts such as precious metals [436–439], transition metal oxides [440], alkaline metal oxides [441], perovskite-like type oxides [442–446], and ceria-based oxides [285,447,448] have shown good catalytic activities for simultaneous removal of NO_x and soot. Especially, CZO is one of the key components owing to its excellent OSC property and robust stability [156,214].

4.6.1. Effect of preparation conditions

The key features of CZO that exhibited the catalytic performance of the simultaneous removal of NO_x and soot were investigated by Bueno-Lopez *et al.* [449]. The catalytic activity of the catalyst for soot combustion was dependent on both specific surface area and Ce/Zr molar ratio, which closely depended on the preparation procedures, but NO_x conversion was very low. The surface distribution of cations was associated with the homogeneity of CZO according to the different synthesis procedure. The specific surface area of CZO was usually lower than 90 m^2/g . Nevertheless, constant T_{50} could be obtained for the catalysts with specific surface areas above this value, i.e., there was a minimum temperature that could be lowered by increasing the surface area of the catalyst (Fig. 24).

The effect of the cerium precursor salt on the catalytic activity of CZO for the removal of NO_x and soot was reported by García-García *et al.* [450]. CZO prepared with $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ showed higher catalytic activity than the counterpart catalysts prepared with a $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ precursor, and ceria-rich catalysts with ceria-rich exhibited better catalytic performance than the corresponding zirconia-rich ones.

4.6.2. Effect of rare earth doping

The property of CZO can be adjusted by dopants, and thus their catalytic activity for the elimination of NO_x and soot is enhanced. Dulgheru *et al.* [451] studied the effects of rare earth (La, Nd, Pr)-modified CZO for catalytic removal of NO_x and soot. The rare earth dopants increased the activity of CZO. Especially, the doping of La and Pr significantly enhanced the low-temperature activity due to the increased formation of NO_2 . Whereas, the effect was less pronounced for a Nd-doped sample. Bueno-López *et al.* [452] investigated the effect of Nd

Fig. 24. T_{50} versus BET surface area of the catalysts for the removal of NO_x and soot. Reprinted from [449] with permission.

doping on the physicochemical properties and catalytic activity for the elimination of NO_x and soot over CZO. Four oxides including CeO_2 , $\text{Ce}_{0.9}\text{Nd}_{0.1}\text{O}_2$, $\text{Ce}_{0.73}\text{Zr}_{0.27}\text{O}_2$, and $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$ were prepared by a CP method. $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$ showed the best catalytic activity due to the improved thermal stability and redox properties. Moreover, it was confirmed that the higher activity of $\text{Ce}_{0.64}\text{Zr}_{0.27}\text{Nd}_{0.09}\text{O}_2$ was closely related to the formation of less stable surface nitrates and nitrites species. Thus, it provided alternative and faster NO_2 production pathways.

4.6.3. Effect of transitional metal doping

It is generally accepted that reaction pathways for the combustion of soot over CZO-supported active metal catalysts can be divided into two sections according to different temperatures. At low temperatures, soot is directly oxidized by active oxygen species that are migrated from the surface of CZO-supported catalysts. At high temperatures, both NO_2 and active oxygen species promote soot oxidation, and especially NO_2 as an intermediate reactant plays a dominant role. In this process, NO_2 serving as the oxidizer is reduced, and soot acting as the reducer is oxidized. Thus, the simultaneous removal of soot and NO_x is realized. However, it is noted that only a part of

NO can be oxidized to NO_2 by the catalyst owing to the thermal equilibrium compositions. Therefore, most of NO is not reduced and directly emitted to atmosphere, which can result in great harmful to human health. Thus, an additional reductant needs to be added into this reaction process. Based on this consideration, Cheng *et al.* [181,182,184] prepared a Fe-doped 3DOM CZO material that could simultaneously remove soot and NO_x from diesel engine exhausts. Ammonia was used as a reductant for NO_x removal. 3DOM Ce-Zr-based mixed oxides were synthesized by a carbon-template method and varied Fe content in the mixed oxide. Those materials showed high efficiency in simultaneous removal of NO_x and soot in intermediate temperatures (285–420 °C with 100% NO_x conversion), which essentially meets the demand of diesel engine exhaust emissions. Moreover, the addition of Fe to Ce-Zr lowered the temperature of soot combustion to a level that was typically achieved by more expensive Pt catalysts (Fig. 25). The importance of the open 3DOM texture in soot capture and combustion was demonstrated by comparison to a mesopore or particle mixed oxide of the same composition. Furthermore, DFT calculation was used to understand the surface reducibility of the mixed oxides and gain insight into the role of Fe and surface oxygen vacancies in the reaction mechanism of NO_x reduction and soot oxidation. It showed that substitution of Fe in CZO increased the number of oxygen vacancies (Fig. 26), thereby enhancing the catalytic performance of simultaneous removal of NO_x and soot. Ce/Zr ratios affected the catalytic activity [181]. A 3DOM $\text{Ce}_{0.85}\text{Fe}_{0.1}\text{Zr}_{0.05}\text{O}_2$ sample exhibited the optimal catalytic activity with a maximum concentration of CO_2 at 415 °C and nearly a 100% NO conversion in the range of 365–503 °C. In addition, 3DOM $\text{Ce}_{0.8}\text{M}_{0.1}\text{Zr}_{0.1}\text{O}_2$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}$) catalysts were also prepared, and the 3DOM $\text{Ce}_{0.8}\text{Mn}_{0.1}\text{Zr}_{0.1}\text{O}_2$ catalyst displayed the maximum concentration of CO_2 at 402 °C for soot combustion and excellent NH_3 -SCR performance at 374–512 °C [183]. The specific 3DOM architecture, high $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio and amount of chemisorbed oxygen species, good low-temperature reductive property, and the abundant of acid sites should be responsible for the excellent catalytic efficiency of $\text{Ce}_{0.8}\text{M}_{0.1}\text{Zr}_{0.1}\text{O}_2$ ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) for the simultaneous elimination of NO_x and soot.

Fig. 25. CO_2 concentration (left) and NO conversion (right) as a function of temperature upon exposure of 3DOM $\text{Ce}_{0.9}\text{Fe}_x\text{Zr}_{0.1}\text{O}_2$ catalysts loosely mixed with model soot. Reaction conditions: 1000 ppm of NH_3 , 1000 ppm of NO , 3% O_2 and balance N_2 , GHSV = 25000 h^{-1} . Reprinted from [182] with permission.

Fig. 26. (a) Structure of Fe-doped $\text{CeO}_2(111)$ as the stoichiometric surface and with one and two oxygen vacancies; (b) Adsorption of NH_3 and NO on Fe-doped $\text{CeO}_2(111)$ with one oxygen vacancy ($\text{Fe}_1\text{Ce}_{1-x}\text{O}_{2-y}(111)$); Fe-doped $\text{CeO}_2(111)$ with the oxygen vacancy preadsorbed by O_2 ($\text{O}_2^*\text{Fe}_1\text{Ce}_{1-x}\text{O}_{2-y}(111)$). Color scheme: white, Ce^{4+} ; green, Ce^{3+} ; red, O; orange, O to be removed; purple, Fe; blue, N; bright white, H. Reprinted from [182] with permission.

4.7. Three-way catalytic removal for the exhausts from gasoline engines

Nowadays, three-way catalysts consisted of noble metals (Pt, Rh, Pd), sub-catalysts (CeO_2 , $\text{CeO}_2\text{-ZrO}_2$, etc.), and monolithic ceramic supports (alumina, $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$, etc.) comprise the state-of-the-art gas after-treatment technology, which are installed in gasoline-powered vehicle emission control systems for simultaneous conversion of CO, NO_x and unburnt HC [453]. Improving performance of catalysts for vehicle exhaust is the key issue to meet the increasing standard of emission regulations. Many research groups have pioneeringly and deeply studied the properties of CZO and its important role in three-way catalysis [454–459]. It has been found that the preparation process [460–462] and material composition [463–466] can significantly influence the concentration of active Ce^{4+} species and structural properties in the solid solution, as shown in Table 9.

4.7.1. Effect of preparation conditions

Zhou *et al.* [467] investigated the effect of synthesis conditions (pH values of the solution of metal precursors and aging temperature) on properties of $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$ prepared by a CP method and its application in Pd-based TWCs. The crystallite size of CZO increased significantly with increasing aging temperature during precipitation, while OSC dropped and no notable effect on porosity of CZO was observed. Moreover, the structural properties of CZO were affected by the pH value during precipitation. Pd-based TWCs supported on this CZO support showed the best catalytic activity. Chen *et al.* [468] investigated the effect of synthesis methods (CP, mechanical mixing, and modified CP method) on the structural properties and catalytic performance of Pd/ $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2\text{-Al}_2\text{O}_3$ TWCs. The different preparation methods gave rise to the different inter-

actions between CZO and Al_2O_3 , thereby leading to various atom rearrangements during the aging process. The catalyst prepared by the modified CP method maintained superior textural and structural properties as well as reductive behavior after being aged, which exhibited high catalytic performance with 10% conversion temperatures of C_3H_8 , CO, and NO of 327, 164, and 208 °C, respectively. These were obviously lower than that of the catalysts synthesized by the conventional CP method and mechanical mixing route. Hu *et al.* [7] synthesized nanosize CZY using a hydrothermal method. TWCs-containing CZY displayed a higher catalytic activity. Zhang *et al.* [469] prepared $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0\text{--}0.8$) nanoparticle powders by a mild urea hydrolysis hydrothermal method. $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0.4\text{--}0.6$) powders preferred a metastable t'' phase to t' phase due to small crystallite size effect. The stabilization of pseudocubic t'' structure led to the high strain level in $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0.4\text{--}0.6$) crystal lattice. Moreover, a linear relationship between the lattice strain and OSC value of the $\text{CeO}_2\text{-ZrO}_2$ catalyst was observed, and this correlation could be used as a tool to evaluate its OSC and help to fabricate new $\text{CeO}_2\text{-ZrO}_2$ catalysts with higher OSC and better redox performance. Zhou and co-workers [470] reported the effect of mechanical mixing and CP methods on the redox behavior and catalytic performance of the three-way CZA catalysts. CZA prepared by the CP method exhibited better thermal stability than that prepared by mechanical mixing due to the presence of stronger interaction between CZO and Al_2O_3 , which was helpful for maintaining large surface area and small particle size and inhibiting the formation of α -alumina phase under the high-temperature condition. Moreover, it could also improve the thermal stability of Pd/CZA catalysts. They further studied the preparation methods (CP, homogeneous precipitation, ME and hydrothermal method) on the catalytic performance of $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$ -supported Pd TWCs [471]. The preparation methods significantly influenced the physicochemical properties of $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$ mixed oxides. The catalyst prepared

Table 9

Catalytic activities of nanosize CZO materials in three-way catalytic removal.

Three-way catalyst	Reaction conditions	T_{50} (°C)				Ref.
		HC	CO	NO	NO ₂	
Ce _{0.68} Zr _{0.27} Nd _{0.05} O ₂	NO/C ₃ H ₆ /C ₆ H ₆ /CO/O ₂ /CO ₂ /H ₂ O/GHSV = 0.1:0.012:0.018:0.03:5.3/2/42000 h ⁻¹	520	—	—	—	[492]
Pd/Ce _{0.2} Zr _{0.8} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	230	160	232	180	[489]
Pd/5%La-Ce _{0.2} Zr _{0.8} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	215	181	213	187	[485]
Pt/La _{0.1} Ce _{0.4} Zr _{0.5} O _{1.9} -Al ₂ O ₃	NO/C ₃ H ₆ /CO/O ₂ /GHSV = 1:1.067:7.78/50,500 h ⁻¹	350	333	370	—	[487]
Pt-Rh/Y _{0.075} La _{0.075} Ce _{0.35} Zr _{0.50} O ₂ -Al ₂ O ₃	NO/C ₃ H ₈ /CO/O ₂ /CO ₂ /H ₂ O/GHSV = 0.1:0.05:0.72:6.21:10:8.33/34000 h ⁻¹	222	170	189	—	[488]
Pd/10%Pr-Ce _{0.2} Zr _{0.8} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	200	148	173	156	[489]
Pd/8%Pr-Ce _{0.33} Zr _{0.67} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.25:0.55:0.275:5.6:21/43000 h ⁻¹	250	209	261	212	[490]
Pd/5%Pr-Ce _{0.2} Zr _{0.8} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	212	155	178	158	[489]
Pd/5%Nd-Ce _{0.2} Zr _{0.8} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	218	184	206	170	[491]
Pt-Rh/Nd _{0.35} Ce _{0.35} Zr _{0.55} O _{1.95} -Al ₂ O ₃	NO/C ₃ H ₈ /CO/O ₂ /CO ₂ /H ₂ O/GHSV = 0.1:0.081:0.646:6.21:12:10/34000 h ⁻¹	259	160	211	—	[493]
Pd/5%Sm-Ce _{0.2} Zr _{0.8} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	220	178	183	180	[495]
Pd/5%Y-Ce _{0.2} Zr _{0.8} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	233	181	207	181	[495]
Pd/5%Cr-Ce _{0.67} Zr _{0.33} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	280	203	305	235	[502]
Pd/5%Mn-Ce _{0.67} Zr _{0.33} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	279	130	258	182	[502]
Pd/1%Fe-Ce _{0.67} Zr _{0.33} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	252	115	240	126	[496]
Pd/5%Co-Ce _{0.67} Zr _{0.33} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	245	161	210	167	[497]
Pd/5%Ni-Ce _{0.67} Zr _{0.33} O ₂	NO/NO ₂ /C ₃ H ₆ /C ₃ H ₈ /CO/O ₂ /GHSV = 1:0.3:0.67:0.33:7.5:7.45/43000 h ⁻¹	264	161	184	184	[498]

 T_{50} is denoted as 50% conversion temperatures of HC, CO, NO and NO₂.

by the CP method amplified the stoichiometric window for the fresh and aged catalyst due to suitable pore distribution, better OSC value, good redox property, and textural stability.

4.7.2. Effect of pretreatment conditions

Liotta *et al.* [472] investigated the effect of redox pretreatment on the structural composition of CZO for three-way catalysis. The changes of structure resulted from different calcination treatments were brought back by the redox cycles. The reductive behavior of CZO was not changed by repeated cycles, and the loss of surface area did not affect the total OSC. In addition, the alternative reductive and oxidative treatments led to reversible change of the solid solution composition around the nominal value of Ce_{0.6}Zr_{0.4}O₂. Zhou *et al.* [473] found that the catalytic activities of Pd/CZO-Al₂O₃ catalysts were affected by thermal treatment. The surface oxygen desorption capacity and lattice oxygen mobility decreased due to the sintering of supports after being calcined at high temperature, which was unfavorable for the dispersion of active species, leading to the loss of three-way catalytic activities. Anderson *et al.* [474] investigated the effect of oxychlorination treatments on the redox and oxygen storage and release properties of Pd-Rh/CZO/Al₂O₃ model TWCs. Thermal aging could not only lead to the decrease of metal dispersion, but also result in a loss of OSC as oxygen storage component. A series of complex feed-streams were performed on Ce_{0.68}Zr_{0.32}O₂ mixed oxide to investigate its performance as TWCs by González-Velasco *et al.* [475]. The pre-reducing treatment could greatly enhance both low-temperature NO reduction activity and N₂ selectivity. Although a remarkable decrease in the specific surface area of the mixed oxide took place after being aged at 900 °C, the catalytic activity of the aged sample remained similar or even better than the fresh one due to the increased OSC value. Therefore, CO and HC emissions during cold-start state could be reduced by placing the catalytic converter nearer the outlet to the engine exhaust, where the CZO-based catalyst would be heated faster.

4.7.3. Effect of alkali or alkali-earth metals doping

Ba and Sr are reported to be two excellent promoters for Al₂O₃, which can effectively suppress the decrease of specific surface area and inhibit the transformation of the Al₂O₃ phase at high temperature in the three-way catalytic reaction [476–479]. Zhou's group [480] reported the effect of BaO doping on the structure and catalytic performance of Pd/Ce_xZr_{1-x}O₂ ($x = 0.2-0.8$) catalysts for automobile emission control. BaO addition significantly promoted the catalytic activity of HC and NO_x conversions due to promoting the formation of oxygen vacancy and improving active oxygen mobility resulting from electronic and structural modifications. After thermal aging treatment, Zr-rich catalysts (CeO₂/ZrO₂ < 1) underwent less severe deterioration of the catalytic activity compared with Ce-rich catalysts (CeO₂/ZrO₂ ≥ 1) due to better thermal stability, and Pd/Ce_{0.5}Zr_{0.5}O₂BaO presented the optimally catalytic performance. Subsequently, they probed the role of Ba in TWCs Pd/Ce_{0.5}Zr_{0.5}O₂ using in-situ DRIFTS [481]. The introduction of Ba weakened the strong adsorption of HC reactants on the catalyst surface and accelerated NO dissociation. It facilitated the formation of intermediates (CN and NCO) due to the excellent electron-donating ability of Ba. Thereby Ba-modified catalysts exhibited much higher catalytic activity for HC and NO_x conversions than the unmodified one. However, the introduction of Ba led to the loss of active sites, thus it inhibited CO oxidation at low temperatures. Wang *et al.* [482] investigated the effect of different amounts of Sr doping on the catalytic performance of Pd/Ce_{0.67}Zr_{0.33}O₂ catalysts for automobile emission control. Sr doping enhanced the low-temperature activity and the thermal stability of the Pd phase owing to the improved oxygen mobility and OSC. Pd-based TWCs supported on Ce_{0.67}Zr_{0.33}Sr_{0.03}O_{2.03} support exhibited the optimal activity for C₃H₈ and NO conversion as well as broadened activation temperature window. Shi *et al.* [483] conducted a comparative study of the catalytic performance over SrO and BaO doping CeO₂-ZrO₂ for TWCs. Ce_{0.35}Zr_{0.55}Sr_{0.10}O_{1.9} (CZS) and Ce_{0.35}Zr_{0.55}Ba_{0.10}O_{1.9} (CZB) were

prepared by an oxidation-CP method with H_2O_2 as oxidizing agent, and then they were used for preparing TWCs with a low loading amount of Pt and Rh. The incorporation of Sr^{2+} ions into CZO could retain a higher OSC value than the introduction of Ba^{2+} ions. Moreover, the introduction of Sr^{2+} ions favored the formation of homogeneously face-centered cubic phases and maintained the stability of lattice cell units. Therefore, the catalyst modified by Sr^{2+} exhibited a better catalytic activity and wider activation temperature window.

4.7.4. Effect of rare earth doping

With ever increasingly rigorous emission regulations are being implemented, taking into account that a significant portion of toxic emissions is produced during cold start, it is necessary to place TWCs closer to the engine in order to attain their light-off activity immediately after the start up of the engine. Consequently, the catalysts should be capable of tolerating high temperature. Therefore, better thermal stability and higher OSC are urgent for the development of new-generation TWCs. A great amount of research has demonstrated that the doping rare earth metal can improve the three-way catalytic activity and temperature operation window, as shown in Table 9 [484–498].

4.7.5. Effect of transition metal doping

Effect of different amounts of Fe-modified $\text{CeO}_2\text{-ZrO}_2$ on the physicochemical properties and catalytic behavior of TWCs for automotive emission control was investigated by Zhou *et al.* [496,497]. The Pd/CZFe(1%) catalyst exhibited optimal catalytic performance for CO, HC, NO, and NO_2 eliminations. The doping of 1% iron oxide promoted the formation of homogeneous Ce-Zr-Fe-O ternary solid solution, which not only facilitated the reduction of $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ and the generation of oxygen vacancy and then improved the interaction between Fe and Ce-Zr, but also enhanced Ce redox behavior. The introduction of cobalt oxide by the CP method considerably enhanced the catalytic activity of Pd-based TWCs with T_{50} for HC at 245 °C, for CO at 161 °C, for NO at 210 °C, and for NO_2 at 167 °C. It should be due to the formation of more homogeneous ternary solid solution, which improved OSC and the interaction between CZO and cobalt metal. In addition, Zhou *et al.* [498–500] also reported the introduction of Ni promoted the redox behavior of Pd/CZO catalysts, leading to the increase of OSC of samples, and Pd/CZNi(3%) exhibited the optimal catalytic performance compared with other catalysts. Zhou *et al.* [501,502] investigated the behavior of Pd supported on transition metals ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) modified $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$ oxides under stoichiometric $\text{CO} + \text{HC} + \text{NO}_x + \text{O}_2$ reaction conditions. The incorporation of transition metals especially Fe and Co strongly improved the oxygen mobility and greatly enhanced the OSC of CZO and the corresponding catalysts. The introduction of Fe and Co into CZO was more beneficial to forming homogeneous Ce-Zr-M-O ternary solid solution and therefore promoting the reduction of Pd/CZO. As a result, the catalytic activities of the catalysts were significantly enhanced (Fig. 27).

4.7.6. Mechanisms of three-way catalytic removal for the

exhausts from gasoline engines over nanosize ceria-zirconium-based solid solutions

Shi *et al.* [483] proposed that the mechanisms of three-way catalytic removal for the exhausts from gasoline engines on Pt-Rh/ $\text{Ce}_{0.35}\text{Zr}_{0.55}\text{Sr}_{0.10}\text{O}_{1.9}$ /La-stabilized Al_2O_3 (LA) and Pt-Rh/ $\text{Ce}_{0.35}\text{Zr}_{0.55}\text{Ba}_{0.10}\text{O}_{1.9}$ /LA were as follows:

The first three steps (Eqs. (53)–(55)) were involved in the elimination of pollutants over TWCs. The fourth step (Eq. (56)) played a role in adjusting the ratio of oxidant/reductant. The last step referred to the reduction of NO_x in TWCs at $\lambda < 1$. Steam-reforming and water-gas shift reactions would take place when H_2O was present in exhaust gas. H_2 would be produced to react with NO. CZO could supply active oxygen species resulting from the cerium charge transformation $\text{CeO}_2 \leftrightarrow \text{Ce}_2\text{O}_3$ when alkaline-earth metal oxides were incorporated to CZO lattice. They would react with the adsorbed NO on the catalyst:

Subsequently, NO_2 reacted with alkaline-earth metal oxides, for example SrO and BaO:

Then $\text{BaO} \cdot \text{NO}_2$ reacted with NO and produced nitrite:

Furthermore, nitrite further reacted with NO_2 and produced nitrate:

Excess oxygen was stored in CZO materials (Eq. (56)) at $\lambda > 1$ based on the former step. Meanwhile, NO_x was also stored in CZO materials, and then released at $\lambda < 1$ and reduced on the noble metal sites, leading to the enhancement of NO_x conversion under wider air/fuel ratios.

4.7.7. Summary of cerium-zirconium-based material for three-way catalytic removal of exhausts from gasoline engines

There are two kinds of oxygen vacancies in cerium-base materials. One is produced by the revivification of Ce^{4+} through Eq. (62), and the other is produced by doping ions through Eqs. (63) and (64) [503–505]. The OSC and redox properties of a cerium-based oxygen storage material are closely related to the oxygen vacancy concentration, migration rate of oxygen vacancy, surface area, and the formation of anion defects [506,507]. The lattice defects formed in the bulk of CZO can make the bulk lattice oxygen and oxygen vacancies to be used in catalytic reaction, but the OSC and thermal stability still can not meet the ever increasingly stringent emission standards. Thus, it urgently needs to further improve oxygen vacancy, lattice defect, OSC, and thermal stability of CZO. The introduc-

Fig. 27. Conversion of (a) HC, (b) NO, (c) CO, and (d) NO₂ over various catalysts as a function of reaction temperature under stoichiometric CO + HC + NO_x + O₂. Reaction condition: NO(0.1%)-NO₂(0.03%)-C₃H₆(0.067%)-C₃H₈(0.033%)-CO(0.75%)-O₂(0.745%) in Ar. Reprinted from [502] with permission.

tion of a third metal to the CZO material may be a feasible way. The influence of extra metal doping mainly includes the following two aspects. One way is to change the radius of dopant ions to make the lattice atoms rearrangement and crystal structure producing different degrees of distortion, which can effectively reduce the diffusion resistance of oxygen in crystal lattice. The other way is to introduce a valence state lower than Ce⁴⁺ and Zr⁴⁺ cation and by the charge balance of crystal lattice to form oxygen vacancy and then improve the diffusion rate of bulk oxygen.

4.8. Nanosize cerium-zirconium-based solid solutions for CO₂ transformation

The emission of CO₂ originated from human activity is a significant factor resulting in the rapid global warming. The catalytic transformation of CO₂ into useful stuffs is recognized to be one of the economic and effective ways to mitigate CO₂ buildup [508]. The key challenge is to develop an effective catalyst that can achieve a high CO₂ conversion at low temperature. Among the catalysts, CZO is one of the key components owing to its excellent OSC property and robust stability. And this part mainly focuses on three CO₂ transformation reactions over CZO: methanation, reforming and chemical transformations.

4.8.1. CO₂ methanation

CO₂ methanation is a green and promising method for the

atmospheric CO₂ reduction. This process is a catalytic hydrogenation reaction (Sabatier reaction):

Much research has been devoted to this particular reaction over Ni-based CZO catalysts. Roger and co-workers [509,510] reported that the Ce/Zr ratio and Ni loading distinctly affected the catalytic performance of Ni/CZO catalysts for CO₂ methanation. The catalyst with Ce/Zr mole ratio of 72/28 and 10% Ni exhibited the best activity. Kawi *et al.* [511] proposed that the preparation methods can influence the catalytic activity of CO₂ methanation over Ni/CZO catalysts. The catalyst prepared by ammonia evaporation showed a higher activity than the counterpart catalysts synthesized by impregnation and deposition precipitation methods due to stronger metal-support interactions between Ce and Ni species. Roger *et al.* [509] also found that noble metals (Rh, Ru) doping significantly enhanced the catalytic performance of Ni/CZO catalysts for CO₂ methanation due to the higher dispersion of Ni species. Wang *et al.* [512] investigated the effect of Ru doping amount on Ni/CZO catalysts for CO₂ methanation. Ru promoted the catalytic activity of catalyst for CO₂ conversion and the catalyst with 3 wt% Ru showed the optimal activity with CO₂ conversion and methane selectivity of 98.2% and 100%, respectively. Zhang *et al.* [513] proposed that the addition of 5 wt% Co can increase the oxygen vacancy and defect of Ni/CZO catalysts, and thereby promote the catalytic activity for CO₂ methanation.

Although the reaction of CO₂ methanation is a simple pro-

cess, it appears to be difficult to reach a consensus on the reaction mechanism. The main controversy concentrates on the nature of intermediate compound and the formation scheme of methane. Kawi *et al.* [511] proposed that the mechanism of CO₂ methanation on Ni/CZO catalyst was as follows. At temperature below 150 °C, CO₂ first adsorbs on the surface of Ni/CZO as mono- and/or bi-dentate carbonate, and then these carbonate species react with dissociated hydrogen to form hydrogenated carbonates. When the temperature is above 250 °C, these hydrogenated carbonate species further react with dissociated hydrogen to generate monodentate carbonate. These intermediate species convert into formaldehyde-like and methoxy species followed by dissociating to CH₄. The methanation of CO₂ proceeds by CO₂ direct hydrogenation to form methane without the formation of CO as intermediate.

4.8.2. Reforming with CO₂ and methane

CO₂ reforming of CH₄ to synthesis gas is considered to be an efficient and attractive approach to eliminate green house gases. This process is called dry reforming of methane reaction:

Idem *et al.* [514] investigated the catalytic activity of Ni-based CZO catalysts for CO₂ reforming of CH₄. Compared with Ni/ZrO₂ and Ni/Ce-doped ZrO₂ catalysts, Ni/CZO showed higher resistance to carbon deposition due to its enhanced low-temperature reducibility. It is well known that the deactivation of catalyst induced by active metal sintering is a thorny and challenging subject in this reaction. Wang and co-workers [515] prepared a series of mesoporous CZO-supported Ni catalysts by a CTAB-assisted method. The catalyst exhibited outstanding stability and initial activity for CO₂ reforming of CH₄ reaction. It should be attributed to its large specific surface area and high dispersion of NiO. Liu *et al.* [516] synthesized a Ni/CZO/MSU-H catalyst by a hydrothermal method for CO₂ reforming of CH₄. Owing to the enhanced OSC for the synergistic effect between MSU-H and CZO, Ni/CZO/MSU-H presented high resistance to coke. In addition, the property of CZO could be adjusted by dopants, thus their catalytic activity for CO₂ reforming of CH₄ was improved. Noronha *et al.* [517] reported that the introduction of Al to CZO could significantly promote the oxygen mobility of the Ni/CZO/Al₂O₃ catalyst, and thereafter it inhibited the formation of carbon from blocking metallic particle. Idem and co-workers [518] studied the effect of metals doping (M = Al, Ba, Ca, Hf, La, Pr, Sm, Sr, Tb, and Y) on Ni/CZMO catalysts for CO₂ reforming of CH₄. The results showed that the dopants increased the activity of Ni/CZMO. Especially, the doping of Ca, La, and Y considerably boosted the low-temperature activity because of the increased Ni dispersion, OSC, and reducibility. Meanwhile, the introduction of a second active metal is another important method to improve the catalytic activity of the Ni/CZO catalyst for CO₂ reforming of CH₄. Lee *et al.* [519] investigated the effect of Mg doping on the physicochemical properties and catalytic activity for CO₂ reforming of CH₄ over Ni/CZO. Ni-Mg/CZO showed better catalytic activity than Ni/CZO due to the improved thermal stability. Moreover, Kiennemann *et al.* [520] studied the influence of the introduction of the second metal (M = Co, Fe, and Rh) on

Ni-M/CZO catalyst activity for CO₂ reforming of CH₄. The addition of Rh distinctly enhanced the activity and stability of the catalyst. In addition to Ni as active species, other metals such as Pt and Co were also supported on CZO and investigated for CO₂ reforming of CH₄ reaction. Resasco *et al.* [521] prepared a series of Pt-based CZO catalysts with different Ce/Zr ratios for CO₂ reforming of CH₄. It was found that Pt/Ce_{0.5}Zr_{0.5}O₂ exhibited an optimal activity and a good correlation between catalytic activity and reducibility. Su *et al.* [52] reported Co-based CZO catalysts with two Ce/Zr ratios (0.33/0.67, 0.6/0.4) for CO₂ reforming of CH₄. The catalyst with the Ce/Zr ratio of 0.6/0.4 showed a better activity due to its better reducibility, higher Co dispersion, and alkalescence of Co/Ce_{0.6}Zr_{0.4}O₂ surface. Meanwhile, it should be noted that Pt- and Co-based CZO catalysts possess a lower activity than Ni/CZO for CO₂ reforming of CH₄. However, the Ni-based catalyst readily induced deactivation due to coke deposition. Thus, the introduction of a second active metal should be necessary.

Idem *et al.* [514,522] proposed that the mechanism of CO₂ reforming of CH₄ on Ni/CZO was as follows:

where, (s) represents the active sites on Ni/CZO surface. CH₄ first adsorbs on S and then dissociates to CH_x fragments. The adsorbed H atoms reacts to produce H₂:

CH_x fragments were oxidated on Ni/CZO surface to form CO and H₂:

Eq. (70) represents the oxidation of reduced sites on Ni/CZO surface by CO₂ to generate CO and initial Ni/CZO. Therefore, the reaction can readily proceed forward by the highly mobile oxygen species supplied by the high OSC and reducibility of Ni/CZO.

4.8.3. CO₂ for the synthesis of dimethyl carbonate

It is generally accepted that dimethyl carbonate (DMC) is an important chemical intermediate in chemical industry and direct synthesis of DMC from CO₂ and methanol is an environmentally friendly chemical process [523]. Tomishige *et al.* [524] employed CZO as a catalyst for the synthesis of DMC from CO₂ and methanol reaction. They found that the catalytic activity of catalyst is closely related to the calcination temperature, and the higher calcination temperature can induce more active surface and thereby enhance the activity. Kim *et al.* [525–527] reported that the catalytic activity of the catalyst for this reaction was dependent on the preparation method and the catalyst prepared by a decomposition method using adipic acid exhibited the highest specific surface area (170 m²/g) and best catalytic performance. Saha *et al.* [528] synthesized a highly active and stable CZO/graphene catalyst for direct synthesis of DMC from CO₂ and methanol. They proposed that the introduction of grapheme significantly promoted the formation of highly crystalline nanostructures and thereby improved its activity. Jung *et al.* [529] prepared a series of Ga₂O₃-modified CZO catalysts and investigated their catalytic activity for direct synthesis of

DMC from CO₂ and methanol. 5 wt% Ga₂O₃/CZO showed the best activity. Jung and co-workers [530] further studied the effect of acidity of catalyst on the catalytic performance for synthesis of DMC from CO₂ and methanol. They prepared PW₁₂O₄₀-modified CZO catalysts for this reaction. The results revealed that the modification of CZO by PW₁₂O₄₀ greatly improved the activity of catalyst for synthesis of DMC from CO₂ and methanol because of the enhancement of Brønsted acid sites provided by PW₁₂O₄₀ and that the acidity played a key role in influencing the catalyst activity. Liu *et al.* [531] for the first time prepared ionic liquid 1-ethyl-3-methylimidazolium bromide ([EMIM]Br)-modified CZO catalyst for synthesis of DMC from CO₂ and methanol. The catalytic performance of [EMIM]Br/CZO increased for DMC production, and it provided a promising alternative for the selective production of DMC from methanol and CO₂.

Kumar *et al.* [532,533] proposed that the mechanism of synthesis of DMC from CO₂ and methanol on CZO was as follows.

CH₃OH first adsorbs on acidic and basic sites of CZO surface and then dissociates to CH₃⁺, OH⁻, CH₃O⁻, and H⁺, respectively:

Then, CH₃O⁻ reacts with CO₂ to form CH₃OCO₂⁻ on the basic sites of CZO:

Finally, CH₃OCO₂⁻ reacts with CH₃⁺ to form DMC, and H⁺ reacts with OH⁻ to generate H₂O:

4.9. Summary of nanosize cerium-zirconium-based materials for environmental catalysis

Environmental catalysis, which can transform pollutants into harmless substances or valuable stuff, is now recognized as one of the most useful methods to reduce environmental pollution in the world [534,535]. CZO is used as the active component, support, or oxygen storage material, and it is indispensable to purify pollutants in environmental catalysis. The main characteristics of environmental catalysts are as follows.

(a) High activity. The catalysts should be extremely efficient to remove the hazardous substances. Because the concentration of the harmful substances in exhausts is usually low, it is only the catalysts with high activity that can efficiently remove them.

(b) High selectivity. The exhaust gas compositions to be disposed are often complex, and the catalysts should possess high selectivity.

(c) High stability. The gases to be treated often contain some toxic ingredients. Therefore, the catalysts should have strong toxicity resistance, high chemical stability, and long lifetime. Moreover, the catalysts should have high thermal stability and wide operation temperature window.

(d) High adaptability. The reaction conditions for the re-

moval of harmful substances vary dramatically. For example, the space velocity of automobile exhausts could be as high as hundreds of thousands, and the changes of the exhaust temperature vary from dozens of Celsius degrees when cold starting to seven or eight hundred Celsius degrees when speeding up.

In addition, the environmental catalysts should also possess high mechanical strength, because the amount of gases to be treated is often large. The catalysts ought to withstand the pressure of fluid flushing. Moreover, the catalysts should be easy to be prepared, cheap and wear-resisting, and low pressure drop.

CZO materials possess good redox and OSC. They are excellent environmental catalysts or acted as the assistant of precious metal catalysts. Although the lattice defects forming in CZO can be helpful to the catalytic reaction, the OSC and thermal stability should be further improved to meet the requirements of environmental catalysts for high activity, high selectivity, high stability and high adaptability. From the typical catalytic reactions described above, it can be deduced that the methods to improve the properties of CZO catalysts are as follows: (1) adopting a suitable preparation method to design and improve the microstructure texture and physicochemical properties of CZO; (2) supporting active metals to enhance catalytic performance of CZO; (3) introduction of additional components into CZO to further increase the degree of lattice oxygen deficiency, improve OSC, and then enhance the catalytic activity, selectivity, and adaptability of environmental catalysts. The addition of additional components including rare earth, transition and alkaline earth or other metals can also inhibit the transformation of crystal phase of CZO and then improve the thermal stability of environmental catalysts.

Doping rare earth oxides with variable state into CZO can not only enhance their lattice defects and improve the redox property of catalyst, but also significantly enhance lattice defects such as the number of oxygen vacancies. Additionally, doping rare earth elements into CZO can also form a ternary solid solution, which may improve the thermal stability of CZO [536].

Transition metals have unfilled valence orbit, and their properties are quite different from other elements. There are many single electrons in the electron configuration of the element in this part, which are readily to lose, so these metals have a variable valence state. The unique electron configuration of transition metals determines their good low-temperature redox properties. The previous reviews show that the introduction of transition metals into CZO can form a solid solution structure and the modified CZO exhibits good low-temperature redox properties. The transition metals supported catalysts possess a low ignition temperature, which realize the purification treatment of automobile exhaust under cold start condition. The common transition metals used for doping CZO are Mn, Cu, Fe, Co, Ni, and Cr, etc.

Alkaline earth metals can form ternary solid solution with CZO to some extent, but the solid solubility varies greatly with the change of ion radius of alkaline earth metals. The ion radii of Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺ are 0.66, 1.12, 1.25, and 1.42 Å, re-

spectively [537,538]. Among them, Ca^{2+} and Sr^{2+} exhibit higher solid solubility with CZO because of their appropriate ion radii, but Mg^{2+} and Ba^{2+} show lower solid solubility with CZO. The effect of doping different alkali earth metals on the catalytic properties of CZO is different. Ca and Sr are easily distributed in the lattice of CZO to form ternary solid solution structure, which can improve the thermal stability and OSC performance of CZO based catalysts.

The oxides of Al_2O_3 and SiO_2 can remarkably affect the catalytic performance of CZO. Although they can not be soluble with cerium and zirconium, they can interact with each other to generate new dispersive phase, which can inhibit catalyst from sintering at high temperature and improve its stability, redox and OSC performance.

5. General conclusions and perspectives

Different from the other rare earth oxides, cerium-zirconium-based solid solutions and related oxides are excellent candidate catalysts for heterogeneous catalysis due to the unique textural and structural properties, controllable composition, and good redox and OSC properties derived from the facile shift of $\text{Ce}^{3+}/\text{Ce}^{4+}$. By partial substitution of ions Ce^{4+} or Zr^{4+} , the amount of nonstoichiometric oxygen and redox behavior of the materials can be changed, which would remarkably enhance the catalytic performance of these materials. Thus, cerium-zirconium-based oxides are widely applied in heterogeneous catalysis especially for environmental catalysis, such as the purification of CO, NO_x , NH_3 , VOC, CO_2 , soot, etc. In addition, the cerium-zirconium-based oxides were also widely used for fuel cells, solar energy materials, and so on.

CZO-based materials are interesting for catalysis applications, and some work should be further attempted to improve the performance of CZO-based catalysts. The basic strategies according the above description include:

(a) Adopting a suitable preparation method to improve the microstructure texture and physicochemical properties of nanosize CZO;

(b) Adjusting the Ce/Zr ratio to promote the redox properties of CZO-based materials;

(c) Supporting active metals, e.g. noble metals Pt, Rh, and Pd or transitional metals Mn, Co, and Cu, etc., to enhance catalytic performance of CZO-based materials;

(d) Introducing additional components to CZO to further increase lattice oxygen deficiency, improve OSC, and enhance the catalytic activity, selectivity, and adaptability of catalysts. The addition of the third component including rare earth, transition and alkaline earth or other metals can also inhibit the transformation of crystal phase of CZO and then improve the thermal stability of catalysts.

Historically, the inventors of CZO materials in the 1970s focused on their application for removal of exhaust gases to substitute the noble metal catalysts. However, this impetus has declined mainly owing to their lower OSC and thermal stability. This weakness certainly warrants further research on the subject. The correlation between catalytic performance and solid state properties is crucial for the design and tailoring of effi-

cient catalysts. CZO materials should be further improved to meet the requirements of environmental catalysts for the high activity, the high selectivity, the high stability, and the high adaptability. It is anticipated that further investigations will expand the understanding for their structure and physicochemical properties and contribute to the development in the practical processes for more widely fields such as catalysis and separation, energy storage and utilization, and optical or aerospace materials.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

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Structure, synthesis, and catalytic properties of nanosize cerium-zirconium-based solid solutions in environmental catalysis

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Cerium-zirconium-based solid solutions have been widely used in environmental catalysis, such as the purification for nitrogen oxides (NO_x), CO, hydrocarbon (HC), CO₂ and solid particulate matters (PM).

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铈锆固溶体的结构、合成及在环境催化领域中的应用

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摘要: 二氧化铈作为一种特殊的立方萤石结构, 是应用最为广泛的稀土氧化物。同时, 它也是一种合适的催化剂载体, 可以促进活性组分的均匀分布, 提高催化活性。但纯二氧化铈在高温下容易发生团聚, 导致比表面积严重降低, 而锆(Zr)掺杂所形成的铈锆固溶体(CZO)会显著提高铈基催化剂的稳定性。在Zr含量较低时, CZO主要呈现立方萤石结构, 随着Zr含量增加, CZO结构逐渐由立方相转变为正方相, 并最终形成单斜相。此外, 与其它稀土氧化物不同, CZO由于其独特的结构性、可控的组成、良好的氧化还原性能以及氧储存性能(OSC)而备受关注。

截至目前, 由于其特殊的物理化学性质和有序的空间形貌, 纳米尺寸CZO格外引人关注。其形貌主要包括纳米粉末、一维纳米棒、纳米管、纳米带、纳米线、二维纳米薄膜、三维纳米笼、三维介孔、大孔和多级孔。基于其不同的形貌及有序的空间结构, CZO材料呈现不同的性质, 并且已被广泛应用于多相催化领域。然而, 不同形貌CZO材料的性能仍然有进一步提升的空间, 例如: 提高材料的稳定性及机械强度; 探索环境友好型合成路径; 考察反应时间、温度、溶液pH值、Ce和Zr源的浓度和构型、金属掺杂等对形貌的影响; 研究不同形貌CZO纳米材料的物理化学性质; 阐明CZO结构、形貌与其催化性能之间的关系。

环境催化可将污染物转化为无害或有价值的物质, 因而被认为是当今减少环境污染最有用的方法之一。而CZO作为活性组分、载体和氧存储材料具有优异的催化活性、较高选择性、高稳定性和极强的适应能力, 是环境催化领域消除污染物过程中必不可少的组分, 因而被广泛应用于催化CO、VOC、Soot、PM和HC燃烧、NO_x选择性催化还原和直接降解、CO₂转化等反应。研究发现: 采用合适的制备方法能够改善CZO的结构和物理化学性质; 调节Ce/Zr摩尔比能促进CZO基材料的氧化还原性能; 负载活性金属如贵金属Pt、Rh、Pd或过渡金属Mn、Co、Cu等可提高CZO的催化性能; 引入第三组分不仅可以增加CZO晶格氧缺陷, 改善其OSC, 进而提高其催化活性、选择性和稳定性, 还可以抑制晶体转变, 提高CZO催化剂的热稳定性。然而, 自1970年代至今, 进一步提高CZO基催化剂的OSC和热稳定性以满足日益严峻的环保要求迫在眉睫。

关键词: 铈锆固溶体; 结构; 合成; 方法; 环境催化

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