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Facile synthesis of catalytically active CeO₂ for soot combustion

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Pure ceria catalysts were prepared by a facile modified homogeneous co-precipitation method, and their catalytic performance was evaluated in the soot oxidation reaction. The structure and textural properties of the synthesized catalysts were characterized via XRD, N₂ adsorption/desorption, TG-DSC-MS, H₂-TPR, FE-SEM, HR-TEM and XPS techniques. It is shown that CeO₂ samples prepared by the improved co-precipitation method exhibit obviously better catalytic activity than those prepared by the conventional co-precipitation method. The CeO₂-CP4-F sample shows the best activity, for which the peak temperature, *T_p*, values of soot combustion are about 465 °C in O₂ stream gas and 430 °C in a NO/O₂ stream under soot/catalyst “loose contact” conditions. Moreover, after high temperature aging, the activity of CeO₂-CP4-A becomes even better, for which the *T_p* value of soot combustion is lowered to 445 °C in O₂ air gas. The catalytic activity is not well associated with the physicochemical properties of BET surface area, particle size and reducibility at low temperatures. The number of lattice oxygen and its mobility in the series of CeO₂ may be the crucial factor to decide the overall catalytic performance. According to the HRTEM result, the excellent migration of lattice oxygen may result from the preferential exposure of more-reactive planes, which may be the essential reason to explain the good performance of CeO₂ catalysts in soot oxidation.

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1. Introduction

In recent years, diesel engines have been considered as promising power sources for vehicles, due to their higher thermal efficiency, lower CO and unburned hydrocarbon emissions, lower cost and longer lifetime when compared with gasoline-fuelled vehicles.¹ However, nitrogen oxides (NO_x) and particulate matter (mainly in the form of soot) as its main emitted pollutants could result in serious environmental and health problems, which limits its widespread application. An ideal way to solve the problem of diesel particulates is the use of a diesel particulate filter (DPF), on which a trap for filtration purposes and a soot particulate oxidation catalyst for trap regeneration are combined to work

together.^{2,3} Therefore, considering that it needs to be efficiently operated under real working conditions, it is important to develop efficient soot oxidation catalysts with two typical characteristics: (1) excellent catalytic activity for soot combustion at a low temperature range (300–400 °C); (2) good thermal stability to be adapted at the accidental hot spot during the regeneration of the DPF, where the working temperature can sharply increase, sometimes as high as 700 °C.⁴

In the past decade, ceria-based catalysts in combination with other metal oxides have received great attention for the oxidation of soot particles.^{5–7} The catalytic performance of mixed oxides strongly depends on the elements incorporated into CeO₂ and the cost is inevitably increased, especially for noble metal dopants. On the other hand, it has been found that single CeO₂ could also act as a catalyst in soot oxidation reactions due to its peculiar oxygen storage capacity and redox properties (Ce⁴⁺/Ce³⁺).^{8–10} Moreover, additional advantages, such as high thermal stability and few chemical weaknesses, make CeO₂ an ideal catalyst or support. Therefore, a certain effort has been made to focus on investigating the catalytic performance of CeO₂ in soot oxidation and the relationship between activity and physicochemical characteristics has also been deeply studied. The obtained results have proven that CeO₂ with different shapes and morphologies exhibits completely different catalytic performances.^{11–13} The

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reason is that the dominated crystallographic orientation and exposed crystal surfaces is closely related to the morphologies and this in turn could strongly influence the surface atom densities, electronic structure, and chemical reactivity. These properties may ultimately dominate the catalytic activity. Whereas, it was found that the catalytic performance and thermal stability of pure CeO_2 is not good enough to be used under real conditions, for which the T_p value for soot combustion is always higher than 500 °C when the soot and catalyst are under “loose contact” in O_2 gas conditions.^{11,13} Exceptionally, in work by Aneggi *et al.*, pure CeO_2 with a nanorod shape structure exhibits relatively good activity for soot oxidation with $T_p = 485$ °C.¹² However, the activity worsens after high temperature aging. Additionally, a multistep synthesis process was carried out, in which hydrothermal treatment was requested. Meher *et al.* reported a non-hydrothermal method to synthesize CeO_2 with uniform nanorod and nanoflower morphologies, but surfactant (CTAB) is needed.¹¹ Therefore, it is meaningful if pure CeO_2 with a high catalytic performance and excellent thermal stability could be developed *via* a facile synthesis method with low cost and easy operation.

In this article, we employed a modified homogeneous co-precipitation method to synthesize CeO_2 particles with a flaky nanostructure. The results showed that the activity of soot oxidation could be significantly improved over CeO_2 prepared by a modified co-precipitation method compared to that prepared by conventional methods. The effect of high temperature calcination and air conditions on catalytic activity was also investigated. In addition, the serial CeO_2 catalysts were characterized in detail by various techniques. Possible reasons for the high activity of CeO_2 for soot oxidation have been proposed and discussed to develop a basic material concept for designing active CeO_2 catalysts for soot combustion.

2. Experimental

2.1. Catalyst preparation

A series of pure ceria was prepared by a modified homogeneous co-precipitation method. For all samples, the $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, which was bought from the Ruijie Company in Shanghai, was taken as the Ce precursor. Typically, a metal salt solution was prepared by dissolving $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ into 50 mL de-ionized water. Then, different amounts of HNO_3 solution was added and vigorously stirred for 1 h to form homogeneous acidic cerium nitrate solutions. A basic solution with 0.4 M NaOH and 0.4 M Na_2CO_3 as precipitants was prepared in another beaker. It is believed that the HNO_3 added to the metal precursor solution could influence the precipitation process. Both solutions were simultaneously dropped into a separate beaker keeping $\text{pH} = 10 \pm 0.5$ under violent stirring for 2 h, then followed by filtration of the precipitate, washing with de-ionized water till the pH of the filtered water reached 7, and drying in an oven at 60 °C overnight. Finally, the ceria samples were calcined under an air atmosphere at 450 °C (fresh samples) and 750 °C

(aged samples) for 6 h with a heating rate of 1 °C min^{-1} . Fresh samples with different $\text{HNO}_3/\text{Ce}(\text{NO}_3)_3$ molar ratios (0, 0.5, 1, 2) were denoted as $\text{CeO}_2\text{-CP1-F}$, $\text{CeO}_2\text{-CP2-F}$, $\text{CeO}_2\text{-CP3-F}$, $\text{CeO}_2\text{-CP4-F}$, respectively. The $\text{CeO}_2\text{-CP4}$ calcined at 750 °C for 6 h was represented as $\text{CeO}_2\text{-CP4-A}$.

For comparison, pure CeO_2 was also prepared by two different conventional methods: that is a direct solid combustion method and a citric acid sol-gel method. To obtain the $\text{CeO}_2\text{-S-F}$ sample, the $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ precursor was directly calcined at 450 °C under an air atmosphere for 6 h with a heating rate of 1 °C min^{-1} . The process to prepare CeO_2 by a citric acid sol-gel method was described as follows: a certain amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was thoroughly dissolved into 50 mL de-ionized water and then citric acid was added with the molar ratio of citric acid/Ce = 1.2. After this, the solution was violently stirred for 4 h at 80 °C, a gel was obtained and dried in an oven at 60 °C overnight. Finally, the sample was calcined in air at 450 °C for 6 h with a heating rate of 1 °C min^{-1} and denoted as $\text{CeO}_2\text{-CA-F}$.

2.2. Material characterization

Low temperature N_2 adsorption/desorption experiments were carried out at -196 °C on a Micromeritics TriStar II 3020 gas absorption analyzer after heat pretreatment at 200 °C for 6 h under vacuum, and the specific surface area was calculated using the BET equation.

X-ray diffraction (XRD) patterns of samples were measured on a Rigaku Ultima IV X-ray powder diffractometer with $\text{Cu K}\alpha$ radiation, and a working voltage and current of 40 kV and 40 mA, respectively. The average particle sizes of catalysts were estimated using Scherrer's equation.

The reduction behavior was measured by temperature-programmed reduction (TPR) experiments with an AutoChem II 2920 instrument (Micromeritics) using 5 vol.% H_2/Ar as the reducing agent. 50 mg catalyst was loaded in a quartz tube reactor ($\varnothing 10$ mm), and a $\text{H}_2\text{-Ar}$ mixture gas of 40 mL min^{-1} was used with a heating rate of 10 °C min^{-1} from 100 °C to 1000 °C. Prior to the reduction, the metal oxide catalyst (50 mg) was pretreated at 200 °C in Ar for 1 h. The H_2 consumption was monitored on line by a TCD detector.

Thermal gravimetric analysis (TGA) was performed using a thermo-gravimetric analyzer (NETZSCH STA 449 F3) instrument with a MS detector (QMS403C) under air stream to investigate the thermal decomposition of oven-dried CeO_2 precursors. The samples were heated in an air stream at a heating rate of 10 °C min^{-1} to 800 °C, with the flow rate fixed at 40 mL min^{-1} .

Oxygen storage capacity (OSC) of all CeO_2 samples was measured at 400 °C by carrying out TGA experiments in 5 vol.% $\text{H}_2\text{-Ar}$ mixture with a flow of 50 mL min^{-1} , which followed the literature.¹⁴ Firstly, each sample was pretreated in an Ar atmosphere for 1 h at 280 °C, followed by heating at a constant rate (10 °C min^{-1}) up to 400 °C and kept at this temperature for 15 min to eliminate the adsorbed water. Finally, the $\text{H}_2\text{-Ar}$ mixture was introduced while keeping the

temperature at 400 °C for 30 min. The observed weight loss is due to the oxygen removal by H₂ to form water, and it can be associated with the total oxygen storage capacity at that temperature.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a Thermo Scientific K-Alpha high performance electron spectrometer, using monochromatic Al K α as the exciting radiation at a constant pass energy of 1486.6 eV. The binding energies (BE) values were calibrated with the signal of contaminated carbon C 1s at 284.6 eV. The spectra were decomposed by using XPSPEAK software (Ver. 4.1). Field emission scanning electron microscopy (FE-SEM) images were recorded using a Hitachi S-4800 microscope. Microstructural characterization by high-resolution transmission electron microscopy (HRTEM) was carried out with a JEM 2100 instrument. Firstly, the samples were dispersed into ethanol with ultrasonic treatment for 10 min and a drop of the suspension was placed on a copper grid for HRTEM observation.

2.3. Catalytic activity

The catalytic activity for soot oxidation was determined using commercially available carbon black powders (Degussa Printex-U, 97.23 wt.% C, 0.73 wt.% H, 1.16 wt.% O, 0.19 wt.% N, 0.45 wt.% S). Before catalytic activity evaluation, the soot-catalyst mixture consisting of 5 mg soot and 45 mg catalyst was put together and mixed by a spatula for 2 min for “loose contact”, which is the most representative model of diesel particles flowing through a catalyst filter. In order to reduce the pressure drop and prevent reaction runaway, 50 mg of the soot-catalyst mixture was diluted with 300 mg of silica pellets (40–60 mesh). The catalytic activity was evaluated in a fixed bed microreactor (Φ 8 mm $\times$ 300 mm) at atmospheric pressure in each test. The inlet gas mixture containing 5% O₂ or 500 ppm NO/5% O₂ balanced with Ar was passed through the soot-catalyst-silica mixture with a total flow rate of 200 mL min⁻¹. After the soot-catalyst-silica mixture was pretreated under the reactant gases at 200 °C for 0.5 h to remove the impurity on the catalyst surface, the activity of catalyst was performed by a temperature-programmed oxidation (TPO) with a heating rate of 10 °C min⁻¹ from 200 °C to 600 °C. The outlet gas of CO₂ and CO coming from the reactor was simultaneously analyzed using an on-line gas chromatograph (Shimadzu) with a FID detector. In all TPO experiments, reaction is not stopped until the carbon soot was completely burned off. During the catalytic activity evaluation, little CO product was detected, thus in this article only the CO₂ data was supplied to present the catalytic activity.

Reaction rate measurement was performed using isothermal experiments at 500 °C on TG analyzer, according to the reference reported.¹² Firstly, approximately 12–15 mg of a catalyst-soot mixture (soot/catalyst weight ratio 1/9) was pretreated under an Ar atmosphere for 1 h at 150 °C, then it was heated at a constant rate (10 °C min⁻¹) up to the reaction temperature (500 °C), followed by switching to air gas. The

reaction was sustained for 1 h using the weight loss rate as a measure of the soot oxidation rate. During the experiments, because it is difficult to know the exact initial weight of the soot, the reaction rate was calculated and parallelly compared by choosing the degree of 5 minutes soot conversion, instead of the degrees of the same soot conversion.

3. Results and discussion

3.1. Catalytic performance for soot combustion

The catalytic activity of soot oxidation over different CeO₂ samples prepared by different synthesis methods was evaluated and is shown in Fig. 1. The blank experiment of soot combustion without catalyst was also performed (not shown here) and the temperature attaining the maximal soot combustion was about 590 °C. From Fig. 1, we can see that the soot oxidation could be accelerated with the help of CeO₂. However, over different CeO₂ catalysts, the improvement degree is disparate. In order to simplify the comparison of catalytic activity, the peak temperature (denoted as T_p) of the soot temperature-programmed combustion plot of the outlet CO₂ concentration is taken as an index of the catalytic performance. Under an O₂/Ar air stream, the T_p values of the CeO₂-CP1-F, CeO₂-CP2-F, CeO₂-CP3-F, CeO₂-CP4-F catalysts are 545 °C, 530 °C, 480 °C and 465 °C, respectively. While for the CeO₂-S-F and CeO₂-CA-F samples prepared by conventional synthesis methods, the T_p values are higher at 545 °C and 560 °C respectively. Therefore, it is seen that the series of CeO₂-CP-F catalysts generally exhibits better catalytic activity. Of those tested, the CeO₂-CP4-F sample shows the best catalytic performance. Moreover, we extensively compared the catalytic performance of CeO₂-CP4-F with that of pure CeO₂ reported in the literature, which is listed in Table 1. After comparison, it is found that CeO₂-CP4-F also has an obvious advantage with a lower T_p value evaluated under more rigorous experiment conditions. Moreover, the preparation process in this work is more economic and facile than the

Fig. 1 The catalytic activity of soot combustion over CeO₂ samples prepared by different methods under an O₂ stream.

Table 1 Comparison of catalytic performance over various pure CeO₂ catalysts^a

Preparation method	<i>T_m</i> (°C)	Soot/catalyst weight	Air conditions	Reference
Precipitation method	465	5 mg/45 mg	5% O ₂ , 200 ml min ⁻¹	This work
Precipitation method	575	20 mg/80 mg	5% O ₂ , 500 ml min ⁻¹	15
Precipitation-hydrothermal method	485 ^b	1 mg/20 mg	O ₂ , 60 ml min ⁻¹	12
	505 ^c			
Precipitation/ripening method	533, ^d 552, ^e 537 ^f	5 mg/45 mg	10% O ₂ , 100 ml min ⁻¹	16
Precipitation method	575	20 mg/80 mg	5% O ₂ , 500 ml min ⁻¹	17

^a All of the catalytic performances were evaluated under “loose contact” conditions. ^b CeO₂ with nanorod morphology. ^c CeO₂ with nanocube morphology. ^d CeO₂ with fiber morphology. ^e CeO₂ with flake morphology. ^f CeO₂ with stick morphology.

literature. Therefore, from the above result, it is demonstrated that the acidification of the Ce precursor during the co-precipitation process is beneficial to obtain CeO₂ catalysts with high catalytic performance. In a certain range, the deeper the degree of acidification, the better the catalytic performance of the obtained catalysts. Considering the remarkable performance of the CeO₂-CP4-F sample, more effort was contributed to systematically evaluate its potential when applied under real working conditions.

Thermal stability is an important requirement for a soot combustion catalyst if applied under real working conditions. In the present work, the activity of the CeO₂-CP4-A sample after high temperature aging (750 °C, 6 h) is evaluated and compared with that of CeO₂-CP4-F. From Fig. 2, it is interesting to find that under O₂/Ar gas conditions, CeO₂-CP4-A possesses an even better catalytic performance with a lower *T_p* value (*T_p* = 445 °C). In order to confirm the activity, the used CeO₂-CP4-A catalyst was recycled and evaluated in the soot combustion for a second time. The *T_p* value of the used CeO₂-CP4-A increased to 455 °C, but was still lower than that of CeO₂-CP4-F. Referring to the literature, there are some contradictory results about the effect of calcination temperature on the overall activity of pure CeO₂ samples. In the study by Gross *et al.*,¹⁸ an improved activity is observed over a CeO₂ catalyst with the calcination temperature raised, which is in

line with our result. As for the result by Aneggi *et al.*, the overall activity of CeO₂ with nanorod, nanocube and conventional polycrystalline structures gets worse after high temperature treatment (750 °C).¹² It is known that the calcination temperature is an important factor that influences the physicochemical properties of the catalysts, which may lead to different impacts on the activity. The reason to explain the positive effect of high temperature calcination on the activity of CeO₂ will be carefully studied later combined with the characterization results.

NO as an inevitable gas under real conditions. Its positive role in soot oxidation is widely reported and is due to the formation of a stronger oxidant NO₂ (NO + O₂ → NO₂) compared to O₂.¹⁹ Therefore, it is necessary to evaluate the catalytic performance of CeO₂-CP4-F and CeO₂-CP4-A samples under a NO/O₂ gas stream. As displayed in Fig. 2, the catalytic activity is greatly improved with the participation of NO. For example, the *T_p* value of CeO₂-CP4-F is 430 °C under NO/O₂ air gas, which is lowered by 35 °C compared with that under O₂ air gas. Moreover, the formed CO₂ concentration is not increased too much in the 390–430 °C range, which may indicate that the soot oxidation rate at 390 °C has become highly efficient. As for the CeO₂-CP4-A sample, the catalytic activity is also greatly enhanced in the presence of NO, for which the activity in the low temperature range is obviously better than that of CeO₂-CP4-F. However, after a rapid increase of soot oxidation from 340 °C to 360 °C, the oxidation rate is not promoted very much in the range 360–450 °C, which becomes even slower than that of CeO₂-CP4-F. It is reported that the improvement of NO in soot combustion is closely related to the NO oxidation ability of the catalyst.²⁰ We believe that the dramatic decrease of surface area and the poor redox ability resulted from the high temperature calcination, which will be proven by the following characterization result, may lead to the decrease of the NO oxidation ability of CeO₂-CP4-A. That may be the reason to explain the limited improvement of activity over CeO₂-CP4-A catalyst by NO.

In order to confirm the sequence of the catalytic activity more confidently, TGA experiments of soot combustion under isothermal conditions at 500 °C under O₂ air gas were also carried out. The oxidation curves as a function of time are displayed in Fig. 3. It is clearly exhibited that the sequence of the soot combustion rate under isothermal

Fig. 2 The catalytic performance of CeO₂-CP4-F and CeO₂-CP4-A under NO_x/O₂ or O₂ gas streams.

Fig. 3 The soot oxidation curves of CeO_2 catalysts under isothermal conditions at 500 °C in O_2 gas.

conditions at 500 °C roughly follows $\text{CeO}_2\text{-CP4-A} \gg \text{CeO}_2\text{-CP4-F} > \text{CeO}_2\text{-CP3-F} \gg \text{CeO}_2\text{-CP1-F} > \text{CeO}_2\text{-S-F} > \text{CeO}_2\text{-CA-F}$, which is almost consistent with the result of the TPO experiments. In Table 2, it is clearly shown that the oxidation rates of $\text{CeO}_2\text{-CP4-A}$, $\text{CeO}_2\text{-CP4-F}$ and $\text{CeO}_2\text{-CP3-F}$ are remarkably larger than those of $\text{CeO}_2\text{-S-F}$, $\text{CeO}_2\text{-CP1-F}$ and $\text{CeO}_2\text{-CA-F}$. Furthermore, the oxidation rate of $\text{CeO}_2\text{-CP4-A}$ is twice as quick as that of $\text{CeO}_2\text{-CP4-F}$. Therefore, it is more convincing that the $\text{CeO}_2\text{-CP4-A}$ sample possesses the best catalytic performance. Considering the excellent catalytic activity and good thermal stability, we can conclude that the $\text{CeO}_2\text{-CP4-A}$ sample is an ideal candidate as an active catalyst or support for soot oxidation, especially applied at 350–400 °C in the presence of NO/O_2 .

3.2. Physicochemical properties of the catalyst material

The crystalline structures of all ceria samples were investigated by XRD and the results are shown in Fig. 4. According to the literature,²¹ the diffraction peaks located at 28.8°, 33.0°, 47.5°, 56.5°, 59.0°, 69.5°, 76.8° and 79.3° are attributed to the pure fluorite structure of the (111), (200), (220), (311), (222), (400), (331) and (420) crystalline phases, respectively. Compared to the $\text{CeO}_2\text{-S-F}$ and $\text{CeO}_2\text{-CA-F}$ samples, the

Fig. 4 The XRD patterns of different CeO_2 samples.

diffraction peaks of the ceria samples prepared by the normal or modified co-precipitation method are wider, indicating smaller crystallite particles. As listed in Table 3, $\text{CeO}_2\text{-CP3-F}$ and $\text{CeO}_2\text{-CP4-F}$ possess the smallest crystallites, whose diameters are 6.05 nm and 6.07 nm, respectively. For the $\text{CeO}_2\text{-CP4-A}$ sample, due to the particle sintering which resulted from the high temperature aging, the intensity of the diffraction peaks becomes very sharp and the grain size dramatically grows to 47.18 nm. For all ceria samples, the calculated lattice parameters are close to that reported for bulk ceria (0.54110 nm) for conventional samples.¹²

Table 3 displays the specific surface area (S_{BET}) of various catalysts. It is found that $\text{CeO}_2\text{-S-F}$, $\text{CeO}_2\text{-CA-F}$, $\text{CeO}_2\text{-CP1-F}$ possess a relatively larger S_{BET} , which is in the range of 45.0 $\text{m}^2 \text{g}^{-1}$ –77.1 $\text{m}^2 \text{g}^{-1}$. As for the $\text{CeO}_2\text{-CP2-F}$, $\text{CeO}_2\text{-CP3-F}$, $\text{CeO}_2\text{-CP4-F}$, their S_{BET} is close to each other, which is lower at 22.7 $\text{m}^2 \text{g}^{-1}$ –30.1 $\text{m}^2 \text{g}^{-1}$. While for the aged $\text{CeO}_2\text{-CP4-A}$ sample, its S_{BET} is significantly decreased to 1.8 $\text{m}^2 \text{g}^{-1}$. From the above results, we can conclude that the synthesis method and after-treatment conditions could strongly influence the structural and textural characteristics of the final obtained ceria samples.

In order to reveal the influence of preparation conditions on the nature of the obtained samples, the oven-dried ceria prepared by a co-precipitation method were selected as investigated samples and their thermogravimetric behavior was studied *via* TG-MS technology. From the TG curves (not shown here), no weight loss happens after 400 °C, indicating that the calcination temperature choice of 450 °C for 6 h in our experiments is reasonable. The DTG-MS patterns are shown in detail in Fig. 5. Generally, for all investigated samples, the characteristic TG curves demonstrate two step weight loss patterns. The first stage located at a low

Table 2 Oxidation rate data for the soot combustion reaction

Samples	T_p (°C)	Oxidation rate _{loose} ($\mu\text{g s}^{-1}$)
$\text{CeO}_2\text{-CP1-F}$	545	0.2979
$\text{CeO}_2\text{-CP3-F}$	480	1.3386
$\text{CeO}_2\text{-CP4-F}$	465	1.7553
$\text{CeO}_2\text{-CP4-A}$	445	3.6892
$\text{CeO}_2\text{-CA-F}$	560	0.1277
$\text{CeO}_2\text{-S-F}$	545	0.3224

Table 3 Textural and structural properties of investigated samples

Catalysts	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Particle size (nm)	Lattice parameter (nm)	OSC ($\mu\text{moles O m}^{-2}$)	TSAO _{cal} ^a ($\mu\text{moles O m}^{-2}$)	Ce ^{3+/b} (%)	T_p (°C)
CeO ₂ -CP1-F	52.6	8.46	0.54110	1.69	5.4	21.71	545
CeO ₂ -CP2-F	22.7	7.87	0.54111	2.44	5.5	12.77	530
CeO ₂ -CP3-F	24.6	6.05	0.54112	4.70	5.4	11.90	480
CeO ₂ -CP4-F	30.13	6.07	0.54110	5.73	5.4	10.58	465
CeO ₂ -CP4-A	1.80	47.18	0.54124	6.94	5.4	15.60	440
CeO ₂ -S-F	77.1	9.63	0.54110	1.97	5.4	26.58	540
CeO ₂ -CA-F	45.0	9.68	0.54113	1.32	5.4	30.76	560

^a The total surface available oxygen (TSAO) is calculated according to ref. 22 considering the average exposure of the (100) + (111) + (110) surfaces. (100) surface, cubic structure: four atoms, located at ($a/4$) out of the Ce plane, in (a^2); (110) surface, cubic structure: four atoms, located in the plane, in ($a^2/\sqrt{2}$); (111) surface, cubic structure: two atoms, located ($a/3\sqrt{3}$) out of the plane, in ($a^2\sqrt{3}/4$). Assumption that only one oxygen atom out of four is involved in the Ce⁴⁺/Ce³⁺ reduction process. ^b The Ce³⁺ ratio is estimated from the Ce 3d result.

temperature (<150 °C) represents the loss of physically adsorbed water, for which only the H₂O signal is detected by MS.²³ The second one at 200–400 °C may indicate the decomposition of carbonate and hydroxide to ceria oxides, due to the CO₂ and/or H₂O as products. Taking a close look at the DTG curves, it is found that the amount of physically adsorbed water is obviously increased in the sequence of CeO₂-CP4 > CeO₂-CP3 > CeO₂-CP2 > CeO₂-CP1. In addition, judging from the MS results for the second DTG peak, it is speculated that the formed precursor compounds of oven-dried ceria samples are disparate. For the CeO₂-CP1 and CeO₂-CP2 samples, carbonate and hydroxide compounds may coexist (both H₂O and CO₂ as detected products), while for the CeO₂-CP3 and CeO₂-CP4 samples, carbonate is the only existing compound (only CO₂ detected). Furthermore, the decomposition temperature of carbonate is gradually shifted to a high temperature range in the sequence of CeO₂-CP4 >

CeO₂-CP3 > CeO₂-CP2 > CeO₂-CP1. From the TG-MS results, it is proven that the difference of acidification degree during the preparation process has a strong influence on the nature of the ceria precursors, which may predict the different physicochemical properties of the final calcined catalysts.

The reduction of surface and bulk CeO₂ crystals was further studied by hydrogen temperature-programmed reduction and the results are shown in Fig. 6. In line with the results reported in the literature,¹² for all fresh ceria samples, the reduction curves are generally characterized by a bimodal shape with a low temperature peak at *ca.* 450 °C and a large high temperature peak at *ca.* 800 °C, which is attributed to surface and bulk oxide reduction respectively. Making a further observation, it is found that the reduction behavior is obviously distinct. For CeO₂-S-F, CeO₂-CA-F, CeO₂-CP1-F and CeO₂-CP2-F, the proportion of the two reduction peak areas is almost similar with the result in the literature,¹² and relatively the CeO₂-S-F sample possesses the best reducibility with the lowest reduction temperature. As for the CeO₂-CP3-F

Fig. 5 The DTG-MS profiles of oven-dried CeO₂ prepared by a co-precipitation method.

Fig. 6 The H₂-TPR profiles of different CeO₂ samples.

and CeO₂-CP4-F samples, the reduction characteristic looks interesting, for which the reducibility peak located at a high temperature is obviously larger than that for other samples. For the CeO₂-CP4 after high temperature aging (CeO₂-CP4-A), the surface reduction peak almost diminishes due to the sintering, that is, because of crystal growth and surface area decrease, and the strong peak of bulk reduction is still present. The H₂ consumption at different temperature ranges by quantitative analysis is listed in Table 4. It is clearly shown that the sequence of H₂ uptake for the low-temperature reduction peak follows as: CeO₂-S-F > CeO₂-CP1-F > CeO₂-CA-F > CeO₂-CP3-F ≈ CeO₂-CP2-F ≈ CeO₂-CP4-F > CeO₂-CP4-A, which is almost consistent with the order of S_{BET} . This may be because more surface oxygens could be exposed with a larger surface area. For the H₂ consumption at high temperature, it may suggest that relatively more abundant lattice oxygens exist in the bulk of the CeO₂-CP3-F, CeO₂-CP4-F and CeO₂-CP4-A samples and could easily migrate to the surface to be reduced by the H₂ stream, compared to that of CeO₂-S-F, CeO₂-CA-F, CeO₂-CP1-F and CeO₂-CP2-F.

The measurement of oxygen storage capacity (OSC) at 400 °C was carried out and the data is listed in Table 3. The OSC of CeO₂-CA-F, CeO₂-S-F and CeO₂-CP1-F is close to each other, which is 1.32 μmoles O m⁻², 1.97 μmoles O m⁻² and 1.69 μmoles O m⁻², respectively. For the other ceria samples prepared by the improved co-precipitation method, the OSC data is obviously increased. For CeO₂-CP4-F, its OSC is 5.73 μmoles O m⁻², which is the maximal data among the fresh samples. In addition, though high temperature aging for the CeO₂-CP4-A sample could lead to the decrease of S_{BET} and the growth of grain size, the OSC of CeO₂-CP4-A (6.94 μmoles O m⁻²) is increased compared to that of CeO₂-CP4-F. This phenomenon is consistent with the results Aneggi *et al.* reported.¹² On the other hand, the total surface available oxygen (TSAO) is estimated according to the literature reported²² and shown in Table 3. It is seen that all of the ceria samples possess similar TSAO data, which is in the range of 5.4–5.5 μmoles O m⁻². For the CeO₂-CA-F, CeO₂-S-F, CeO₂-CP1-F and CeO₂-CP2-F samples, considering that the OSC data is far less than the TSAO data, it is speculated that OS at 400 °C probably takes place only in the surface. For the CeO₂-CP3-F, CeO₂-CP4-F and CeO₂-CP4-A catalysts, the OSC data is close or even larger than the TSAO data. In these cases, OS is more likely to occur not only at the surface but

also in the bulk. Therefore, from the calculation of OSC and TSAO, it is plausible that the mobility of lattice oxygen in the bulk of the CeO₂-CP3-F, CeO₂-CP4-F and CeO₂-CP4-A samples is better and is more easily desorbed from the catalysts, which is in agreement with the H₂-TPR results.

The XPS characterization was carried out to further investigate the chemical state of the elements existing in the CeO₂ catalysts. The O1s spectra of the CeO₂ catalysts are shown in Fig. 7. According to the literature, for pure CeO₂, the O1s XPS spectra can be resolved into three peaks:^{24,25} lattice oxygen (O_{latt}) at 529–530 eV, surface oxygen (O_{sur}) at 530–532 eV, which is assigned to defect oxide or the surface oxygen ions with low coordination and weakly bonded oxygen species, and adsorbed oxygen species (O_{ads}) at 533–534 eV from hydroxyl species and adsorbed water species as contaminants on the surface. The relative amounts of the surface oxygen species were calculated and are exhibited in Fig. 7. It seems that for the CeO₂ prepared by the co-precipitation method, the proportions of O_{sur} (defined as O_{sur}/(O_{latt} + O_{sur} + O_{ads})) are increased with the order of CeO₂-CP4-F (50.8%) > CeO₂-CP3-F (49.3%) > CeO₂-CP2-F (47.4%) > CeO₂-CP1-F (34.2%). For the CeO₂-CP4-A sample, the proportion of O_{sur} is even higher than that of CeO₂-CP4-F. However, for the reference samples, CeO₂-S-F and CeO₂-CA-F, the proportions of O_{sur} differ a lot, 36.6% and 60.6% respectively. In many catalytic oxidation reactions, the surface oxygen species is beneficial to activate the reaction molecules and facilitate the reaction.^{26,27} There are also some viewpoints that agree with the important role of surface oxygen in the soot combustion reaction. In the report by Aneggi *et al.*, the number of active surface oxygens

Fig. 7 O 1s XPS spectra of the ceria samples.

Table 4 The quantitative TPR analyses of the CeO₂ catalysts

Samples	H ₂ consumption (μmol g _{cat} ⁻¹)	
	Low temperature range	High temperature range
CeO ₂ -CP1-F	0.4668	0.4718
CeO ₂ -CP2-F	0.1978	0.5062
CeO ₂ -CP3-F	0.2043	1.0335
CeO ₂ -CP4-F	0.1939	1.1583
CeO ₂ -CP4-A	0.0015	1.1335
CeO ₂ -CA-F	0.2458	0.4632
CeO ₂ -S-F	0.6208	0.5580

on pure ceria plays a major role in soot combustion under an O₂ gas stream when the soot/catalyst is under “tight contact” conditions.^{14,28} In the present work, a seemingly positive relationship between the proportion of surface active oxygens and the T_p values of soot combustion also exist, except for the CeO₂-CA-F sample. For the CeO₂-CA-F sample, the O_{sur} proportion is very high, but its activity is poor. Here, we think that the O_{sur} itself includes several oxygen species, the nature of which is difficult to clarify. Only part of these surface oxygen species may play roles and participate in the reaction. In addition, the crucial factors that decide the catalytic performance may alter under different soot/catalyst contact situations. Therefore, from the XPS result alone the role of O_{sur} in the soot oxidation couldn't be completely proven.

The complex spectra of Ce 3d are presented in Fig. 8 and fitted into ten components. Referring to the literature, the Ce³⁺ content could be estimated by $Ce^{3+}/(Ce^{3+} + Ce^{4+}) \times 100\%$, where $Ce^{3+} = (u' + u'' + v' + v'')$ and $Ce^{4+} = (u''' + u'' + u + v''' + v'' + v)$. From Table 3, the Ce³⁺ content of the CeO₂ samples is significantly different depending on the synthesis conditions. The general order of Ce³⁺ content follows CeO₂-CA-F (30.76%) > CeO₂-S-F (26.58%) > CeO₂-CP1-F (21.71%) >> CeO₂-CP4-A (15.60%) > CeO₂-CP2-F (12.77%) > CeO₂-CP3-F (11.90%) > CeO₂-CP4-F (10.58%). It is reported that the existence of Ce³⁺ in CeO₂ implies the formation of oxygen vacancies. Therefore, it seems that the fresh CeO₂ prepared by the improved co-precipitation method possess a relatively lower amount of oxygen vacancies. After high temperature aging, the oxygen vacancies of CeO₂-CP4-A are a little increased compared to that of CeO₂-CP4-F.

The morphological properties of three representative catalysts were investigated by FE-SEM, as displayed in Fig. 9. The morphologies of the CeO₂ catalysts exhibit a remarkable

dependence on the preparation conditions. From Fig. 9(A, D), the CeO₂-CP1-F sample possesses a bulky chunk structure, with a relatively rough surface. For the CeO₂-CP4-F in Fig. 9(B, E), a smoother surface with smaller patch morphology is observed. As shown in Fig. 9(C, F), for CeO₂-CP4-A after high temperature calcination, an appreciable change in morphology happens compared with the CeO₂-CP4-F material. The block structure disappeared. Instead, grain particles are formed. According to the literature, morphological change is expected to occur above 500 °C.¹²

Furthermore, these three typical catalysts were carefully studied by HRTEM. The intuitive morphologies of the CeO₂-CP1-F sample are shown in Fig. 10. It is seen that a large and thick agglomerate is still observed after ultrasonic pretreatment, which indicates that the massive structure is combined tightly and difficult to disperse. However, from the low magnification TEM images, homogeneous nanoparticles are its secondary structure. The distribution of the crystallite particles diameter is centered at *ca.* 8–10 nm, which is close to the value of 8.46 nm calculated from the XRD result. The electron diffraction patterns recorded in selected-area mode (SAED) in several regions show smooth rings, which indicate that the CeO₂-CP1-F sample is polycrystalline. The reciprocal spacing of the electron diffraction pattern and their relative intensity indicate cubic CeO₂ is the only crystalline phase, which is in line with the XRD result. The lattice fringes are clearly exhibited. After careful calculation of the space of lattice fringes, it is deduced that the dominant lattice fringes at 3.12 Å correspond to the {111} family.²⁹ In addition, a small part of the (200) crystallographic planes oriented along the [100] direction is occasionally found, at 2.71 Å.

From the HRTEM image of CeO₂-CP4-F in Fig. 11, it is clearly displayed that compared with that of the CeO₂-CP1-F sample, CeO₂-CP4-F possesses smaller fragments with flaky structures, which is more easily dispersed. Similarly, the flaky structure also consists of crystallite nanoparticles. The nanoparticle size is narrower, centered at 6–8 nm, which is almost consistent with the size (6.07 nm) calculated by XRD. Similarly, the CeO₂-CP4-F sample is polycrystalline from the SAED result. After carefully calculation, it is judged that the {111} family is also the main lattice surface, but compared to the CeO₂-CP1-F sample the {100} facets are more frequently found, judging from the representative high magnification TEM images in Fig. 11.

For the CeO₂-CP4-A after high temperature calcination, shown in Fig. 12, an observation by FESEM, large grain particles are the essential structure. No secondary structure existed, which is different from the situation of the CeO₂-CP1-F and CeO₂-CP4-F samples. The nanoparticle size sharply increased to 50–200 nm, which is much larger than the calculation value (47.18 nm) by XRD. Therefore, we believe that high temperature aging could lead to aggregation of the nanoparticles. The SAED result demonstrates that CeO₂-CP4-A prevalently exists in the monocrystalline form. It is reported that after oxidation at high temperature the CeO₂ crystallites preferred to agglomerate to minimize the

Fig. 8 Ce 3d XPS spectra of the ceria samples.

Fig. 9 Representative SEM images of various catalysts: (A, D) CeO₂-CP1-F, (B, E) CeO₂-CP4-F, (C, F) CeO₂-CP4-A.

Fig. 10 HRTEM images of the CeO₂-CP1-F sample.

interface energy with the formation of a lattice-matched coherent interface.³⁰ Furthermore, from the TEM results, it is found that besides the {111} planes, extensive {100} facets in the CeO₂-CP4-A sample are more easily encountered. Typical examples are displayed in Fig. 12. This observation is consistent with the Aneghi *et al.* report,^{12,29} in which it is also observed that more less stable {100} planes could be formed after CeO₂ is subjected to high temperature treatments. It is explained that reactive {100} facets are generated from the favorable formation of an irregular metastable truncated

octahedral structure by aggregation of smaller CeO₂ crystals upon annealing.¹² The preferential plane exposure may be closely related to the catalytic activity.

3.3. Reaction determining factors

After reviewing the literature,^{14,31–33} it was found that there are two prevailing reaction mechanisms of soot catalytic oxidation proposed by authors. One pathway is that soot oxidation could be triggered by the surface active oxygens, such as

Fig. 11 HRTEM images of the CeO₂-CP4-F sample.

Fig. 12 HRTEM images of the CeO₂-CP4-A sample.

superoxide (O_2^-), which may be formed by the gaseous O_2 being adsorbed and activated by the oxygen vacancies. The other possible reaction pathway is that the surface active oxygens come from the bulk by diffusion of lattice oxygen, and then the gaseous O_2 fills the vacant sites to recover the lattice

oxygen afterwards. Although there is little knowledge about the nature of this lattice oxygen species, many authors still believe that the latter reaction mechanism is more important in real soot oxidation over ceria-based catalysts.³¹ In the study by Harada *et al.*, it was proven *via* isotopic exchange experiments

that the soot was firstly oxidized by the abundant lattice oxygen, and then the gaseous O_2 was fed into the bulk and activated to participate in the reaction.³⁴ Bueno-López and co-workers have also carried out soot oxidation with an oxygen isotope at a high temperature of 600 °C, where isotopic oxygen exchange between gaseous O_2 and lattice oxygens of CeO_2 was observed and they concluded soot oxidation was carried out by lattice oxygen.³⁵ Therefore, the existing research result has fully evidenced the peculiar role of lattice oxygen in soot oxidation. Therefore, it is believed that the amount and the diffusion ability of lattice oxygen in the CeO_2 crystal particles will undoubtedly influence the reaction process.

In this work, as for the reason to explain the good activity of CeO_2 -CP4-F and CeO_2 -CP4-A as active catalysts, comprehensive consideration should be made. From the textual parameters, no correlation is found by comparing activity against the BET surface area and particle size. It is noticed that high temperature calcination on CeO_2 -CP4-A leads to the obvious decrease of the BET surface area accompanied by a sharp increase in mean particle diameter, while its catalytic performance is superior to other samples. This result indicates the BET surface area and particle size are not the crucial factors that determine the overall activity, although in the Bueno-López study, the increase of catalyst surface area could explain the improvement of soot oxidation activity, which improves the O_2 -catalyst interaction and the redox properties of the catalyst.³³ In the study by Muroyama *et al.*, it was proposed that the high reducibility at a low temperature range was well associated with the catalytic soot oxidation.² However, here the phenomenon is different. For example, the CeO_2 -CP4-A sample had the best catalytic activity with the worst reducibility at low temperatures, while the CeO_2 -S-F sample had the poorest activity with the best reducibility. Therefore, we think the catalytic activity is not closely related to the reducibility at low temperature in this work. From the XPS results, though the maximal amount of surface oxygen species existed in the CeO_2 -CP4-F and CeO_2 -CP4-A catalysts, their oxygen vacancy number is not great enough. Therefore, it is not scientific to confirm or refute the possibility for soot oxidation caused by the surface oxygen species. On the other hand, from the H_2 -TPR results, the reducibility behavior of lattice oxygen in the high temperature range coincides well with the catalytic performance. As shown in Fig. 13, a positive linear relationship exists between the oxidation activity and OSC data. Therefore, agreeing with the popular viewpoint, the amount of lattice oxygen and its mobility may be the primary factors that determine the catalytic activity. Namely, the soot oxidation proceeds *via* a reaction mechanism caused by the lattice oxygen. Additionally, from the HRTEM result, it is found that the possibility of encountering the (100) facet is increased following the order of CeO_2 -CP4-A > CeO_2 -CP4-F > CeO_2 -CP1-F. As suggested by the literature,³⁶ ceria in the cubic fluorite structure has three low-index planes, *i.e.* the very stable and neutral (111) plane, the less stable (110) plane, and the higher-energy (100) plane. Generally, (100) and (110) planes are more reactive than the

Fig. 13 The dependence of T_p values and OSC.

neutral (111) planes. It is reported that the migration of lattice oxygen from the bulk to the surface on the (110)/(100) facet-dominated catalyst is much easier compared with that on the (111) facet-dominated one.³⁷ Consequently, the preferentially dominating exposed plane may ultimately result in the excellent mobility of lattice oxygen.

Conclusion

A series of pure CeO_2 catalysts was prepared by a modified co-precipitation method and their catalytic performance was evaluated in the soot oxidation reaction. The results demonstrate that the acidification of the precursor during the preparation process helps to improve the catalytic performance of the obtained catalysts. Amongst those tested, CeO_2 -CP4-F shows the best catalytic performance with $T_p = 465$ °C. High temperature calcination of the CeO_2 -CP4-A sample is beneficial to enhance the catalytic activity, with $T_p = 445$ °C. In addition, in the presence of NO/O_2 , the oxidation rate could be further increased, especially in the low temperature range. The characterization results prove that the mobility of lattice oxygen in CeO_2 -CP4-F and CeO_2 -CP4-A is obviously better than in the other samples. The HRTEM result proves that more reactive (100) planes exist in the CeO_2 -CP4-F and CeO_2 -CP4-A samples, which may be the essential reason to explain the good migration of lattice oxygen from the bulk. Finally, it can be rationally anticipated that these CeO_2 oxides can act as effective and promising catalysts or supports in the soot oxidation reaction.

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