两步沉淀法制备耐高温和优异还原性能 CeO$_2$ 材料

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摘要：分别采用两种沉淀方法制备了 CeO$_2$：以传统的氨水为沉淀剂，在氨水沉淀法前引入碳铵沉淀步骤(两步沉淀法)。采用热重–差热(TG-DTA)、傅里叶变换红外(FTIR)、X 光电子能谱(XPS)等手段对沉淀及其分解过程进行了研究。结果表明，在两步沉淀法中的第一步，碳酸物种为主要沉淀物种，而在第二步中被氢氧根取代。X 射线衍射(XRD)和透射电子显微镜(TEM)结果表明，两步沉淀法生成的沉淀颗粒粒径更大。通过两步沉淀法制备的 CeO$_2$ 与氨水沉淀相比具有更好的抗高温老化性能和还原性能。经过 900 ℃焙烧 3 h 后，仍然具有 25 m^2·g^{-1} 和 0.11 cm^3·g^{-1} 的比表面和孔容。

关键词：两步沉淀法；传统沉淀法；耐高温；氧化还原性能
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A Two-Step Precipitation Route to CeO$_2$ Material with Improved Thermal Stability and Reduction Property

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Abstract: Two series of CeO$_2$ samples were prepared by two different synthetic routes: one was conventional precipitation route employing ammonia as reactant, and the other was a two-step precipitation procedure, using ammonium carbonate ((NH$_4$)$_2$CO$_3$) as precipitant at the first step and ammonia as reagent at the second step. The precipitates and their decomposition processes were characterized by thermogravimetric and differential thermal analysis (TG/DTA), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectra (XPS). The results show that the precipitate produced at the (NH)$_4$CO$_3$ precipitation step mainly consists of carbonate species, however, after the second precipitation step by ammonia, the carbonate species are replaced by hydroxyl species. By introducing the intermediate carbonate precipitation process, the nucleation rate of CeO$_2$ can be controlled. X-ray diffraction (XRD) and transmission electron microscopy (TEM) results indicate that the grain size of the precipitate prepared by two-precipitation route is larger than that of the precipitate prepared by conventional route. CeO$_2$ prepared by this two-precipitation route exhibits higher thermal stability and better reduction property than that obtained by traditional procedure. After the heat treatment at 900 ℃ for 3 h, the surface area and pore volume are 25 m^2·g^{-1} and 0.11 cm·g^{-1}, respectively.

Key words：two-step precipitation; conventional precipitation; high thermal stability; redox properties

CeO$_2$-based materials have important roles in many commercial catalytic processes. For example, CeO$_2$ has been used for catalytic wet oxidation [1], for removal of soot from diesel engine exhaust[2] and for fuel cell technology[3]. In addition, they have been one of the most important commercial supports for the purification of exhaust gases [4]. Generally, a three-way catalyst (TWC) is required to simultaneously convert the hydrocarbons, CO and NOx present in the automotive exhaust to harmless H$_2$O, CO$_2$ and N$_2$[5]. However, high conversion of the pollutants can be achieved only when the air-to-fuel (A/F) ratio oscillates around the stoichiometric value (14.6) [5]. Adding of CeO$_2$-based materials can balance the oxygen concentration due to their abilities to store and release oxygen under lean and rich operation conditions, respectively [6]. Under usual TWC working conditions, the above-mentioned performance is essentially related to the surface area of the CeO$_2$ support [7-8]. As soon as significant sintering of CeO$_2$ particles occurs, both redox property and metal-support interactions appear inhibited[9-10]. So, to improve the thermal stability of CeO$_2$-based materials used in TWC is a challenge for researchers and TWC companies.

Different strategies have been used to prepare CeO$_2$-based materials, including precipitation method [11-12], hydrothermal route [13-14], sol-gel techniques [15-16], surfactant-assisted approach [17-18], and combustion synthesis [19-20]. Among these methods, the most convenient one is precipitation. Usually, the precipitation can be carried out via the reaction of cerium (Ⅲ or Ⅳ) salt solution and a base solution such as ammonia [21], ammonium carbonate [22], and alkaline hydroxide[23]. It has been established that, surface area, particle morphology and even the lattice structure of CeO$_2$-based materials are strongly affected by the synthesis conditions [24]. Woodhead [25] firstly developed an H$_2$O$_2$-assitated method based on precipitation method in order to produce CeO$_2$, and after that, the method was adopted by many researchers [26-29]. Investigations have also been carried out by some groups to study the effect of H$_2$O$_2$ on the preparation of CeO$_2$-based materials. Djurii et al [26] found that the presence of H$_2$O$_2$ could change the precursor of CeO$_2$, leading to different decomposition processes. Scholes et al[23,27] investigated the effect of the amount of H$_2$O$_2$ on the physico-chemical properties of precursors and proposed the formation of Ce(O$_2$)(OH)$_2$ on the basis of titration results.

In the present work, we developed a two-step precipitation route based on the H$_2$O$_2$-asistated method to prepare CeO$_2$ material, aiming at preparing CeO$_2$ with improved thermal stability and reduction property. In this two-step route, ammonium carbonate and ammonia were used as reagents at the first and second steps, respectively. The formation process of the sample was also investigated. By introducing an carbonate intermediate precipitation procedure, the crystallite size of the precipitate, as well as the pore size of target CeO$_2$, were enlarged, which are crucial for preparing CeO$_2$-based materials with improved thermal stability and reduction property[28-29].

1 Experimental

1.1 Synthesis

1.1.1 Preparation of precipitate by conventional route

Ce(NO$_3$)$_3$·6H$_2$O was dissolved into distilled water, and H$_2$O$_2$ (30wt%) was added. The molar ratio of Ce(NO$_3$)$_3$:H$_2$O$_2$ was 1:1. A ammonia solution (25wt%) was added into the salt solution to adjust the pH value to 12 under stirring. The obtained precipitate was filtered out and washed with distilled water until no changes in pH value, and dried at 80 ℃ for 5 h to obtain CeC precipitate.

1.1.2 Preparation of precipitate by ammonium carbonate

The preparation procedure was according to experiment (1.1.1), except the base solution was ammonium carbonate (25wt%) and the pH value was adjusted to 8.2. The precipitate was denoted as CeM.

1.1.3 Preparation of precipitate by two-step precipitation route

First, a solution of ammonium carbonate (25wt%) was added into the salt solution prepared according to experiment (1.1.1), till the pH value to 8 under stirring, and kept at room temperature for 2 h. Then an ammonia

solution (25wt%) was added to adjusted the pH value to 12, and then stirred for 12 h. The precipitate was filtered out and washed with distilled water; then it was dried at 80 ℃ for 5 h to produce CeT precipitate.

1.1.4　Calcination of precipitates

The CeT and CeC precipitates were calcined at different temperatures in the range of 500~900 ℃ for 3 h. The target samples were labeled as CeT-t and CeC-t where t stands for the calcination temperature.

1.2　Characterizations

TG/DTA was carried out by a HCT-2 analyzer (Beijing Science Apparatus Factory, Beijing, China) under a flowing N_2 atmosphere (30 mL·min^{-1}). The sample was heated to 600 ℃ with a heating rate of 10 ℃·min^{-1}. The alumina was taken as the reference material.

FTIR spetra were recorded at room temperature in the range of 400~4 000 cm^{-1} using KBr pellet with a Nicolet 6700 FT spectrometer.

X-ray photoelectron spectra data were collected on a XSAM 800 spectrometer (KRATOS Corp.) with a Mg Kα source working at 13 kV and 20 mA, and the C1s peak was used as an internal standard for calculating binding energy values.

The nitrogen adsorption-desorption isotherms were measured on Quantachrome SI instrument. The specific surface areas and pore size distribution were calculated according to Brunauer-Emmett-Teller (BET) method and Barret-Joyner-Halenda (BJH) method, respectively. The measurement was carried out at −196 ℃, after the sample was degassed at 300 ℃ for 3 h under vacuum.

The X-ray diffraction patterns were determined on a D/max-rA diffractometer (RIGAKU Corporation) equipped with Cu Kα (λ=0.154 18 nm) radiation and Graphite monochromator. The anode X-ray target was operated at 40 kV and 25 mA. The X-ray was detected by scintillation counter and recorded for 2θ values between 10° and 80° with a step of 0.03°.

The size of the precipitates was observed with transmission electron microscopy (TEM) using a Tecnai G^2 F20 S-TWIN apparatus operated at 200 kV.

TPR profiles were determined in a conventional reactor equipped with a thermal conductivity detector.

All samples (100 mg) were pretreated in a flow of N_2 at 450 ℃ for 45 min, and then cooled down to room temperature. The reduction was carried out in a flow of 20 mL·min^{-1} of 5% H_2/N_2 from room temperature to 900 ℃ with a heating rate of 10 ℃·min^{-1}.

2　Results and discussion

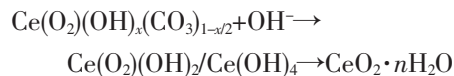### 2.1　Formation processes of precipitates

Composition of the precipitates depends on the kinds of cations and anions present in the solution. In this work, Ce^{3+} is employed as metal salt precursor, while OH^- or CO_3^{2-} is used as precipitants, in the presence of H_2O_2. When ammonia is utilized as precipitant, the following equilibria are expected in the precipitation process[27]:

$$Ce^{3+}+(3/2)H_2O_2+3OH^-\rightarrow Ce(O_2)(OH)_2\rightarrow$$
$$Ce(OH)_4/CeO_2\cdot 2H_2O$$
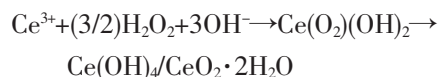
Whereas, in the case of two-step precipitation process, the reaction is very complex since different anions might enter into the precipitate. In the first precipitation step, although the carbonate species is used as reagent, considering the following hydration process[30]:

$$CO_3^{2-}+H_2O\rightarrow HCO_3^-+OH^-$$
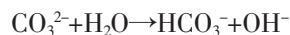
We can reasonably assume that the component of the precipitate is $Ce(O_2)(OH)_x(CO_3)_{1-x/2}$. In the second precipitation step, the OH^- is added, thus the CO_3^{2-} species is entirely replaced by OH^-:

$$Ce(O_2)(OH)_x(CO_3)_{1-x/2}+OH^-\rightarrow$$
$$Ce(O_2)(OH)_2/Ce(OH)_4\rightarrow CeO_2\cdot nH_2O$$

The dehydration process might occur in the operation procedure due to the O_2^{2-} and OH groups are not stable enough[26,29].

Fig.1 presents the thermal behavior of precipitates prepared by different methods. From Fig.1a, we can see that the precipitate prepared by ammonia only shows one continuous decomposition process. The total weight loss is 13.13% , which does not correspond to the decomposition of $Ce(OH)_4$ or $Ce(O_2)(OH)_2$, indicating that the dehydration event has occurred under our operation condition. The DTA curve shows one endothermic peak at about 80 ℃ due to the elimination of physical-adsorbed water [26]. It seems that the
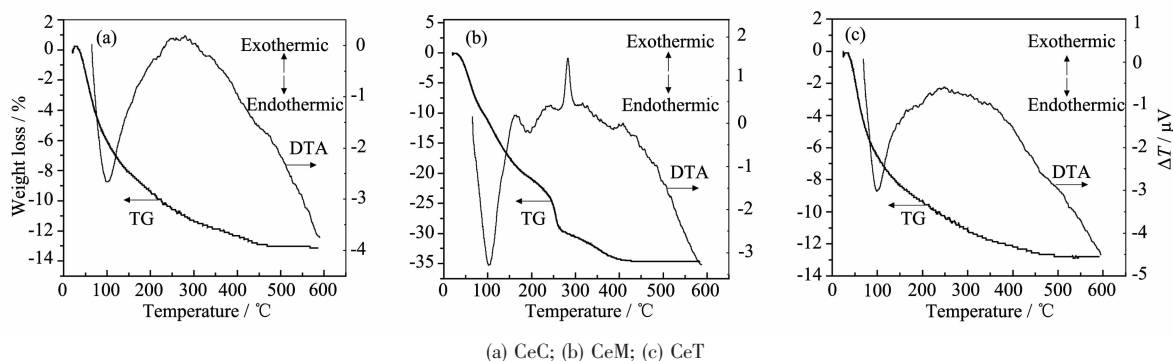
(a) CeC; (b) CeM; (c) CeT

Fig.1　Simultaneous TG/DTA curves of precipitates

crystallization of the hydroxide is a slow process, thus the exothermal phenomenon, as reported in previous study[26], can not be observed. Fig.1b shows the thermal decomposition of the precipitate prepared by ammonium carbonate. The evolution behavior proceeds through three stages at the temperature ranges of 50~200 ℃, 250~350 ℃ and 350~450 ℃, respectively. By comparing with literatures[23,26], we attribute the first one to the desorption of water and the decomposition of O_2^{2-} containing species, and the second one to the crystallization of hydroxide particles, while the last one to the decomposition of carbonate species. Fig.1c displays the thermal events of sample CeT. It is clearly observed that its decomposition process is very similar to that of CeC, indicating they possess the same or similar chemical components. Interestingly, the total weight loss of CeT is 12.7%, which is very close to that of CeC (13%). In addition, the DTA behavior of CeT is also in accordance with CeC, presenting an endothermic peak at about 80 ℃. From the above results, we can conclude that in the second precipitation step of two-step precipitation route, the carbonate species are replaced by OH⁻ groups, indicating the occurrence of following reactions:$Ce(O_2)(OH)_x(CO_3)_{1-x/2}$ $+OH^- \rightarrow Ce(O_2)(OH)_2/Ce(OH)_4 \rightarrow CeO_2 \cdot nH_2O$.

The FTIR spectra for CeO_2 precipitates prepared by different methods are shown in Fig.2. Generally, the intense bands around 3 000~3 650 cm⁻¹ region are attributed to the O-H stretching of H-bound hydroxyl groups or molecularly chemisorbed water[31-32]. The bands at this region of CeC and CeT show three different adsorption signals centered at about 3 540,
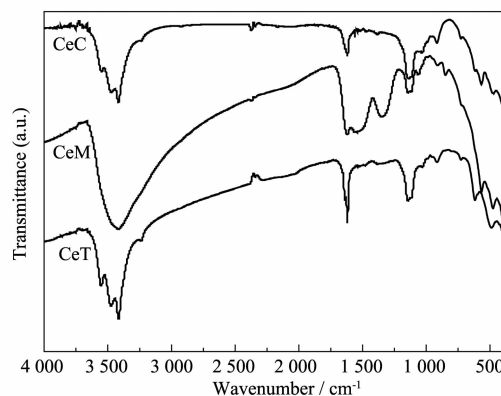

Fig.2　FTIR spectra of precipitates

3 480 and 3 420 cm⁻¹, respectively, indicating the presence of mono-coordinated, bi-coordinated and tri-coordinated hydroxyl groups[31-32]. However, in the case of CeM, only a characteristic broad adsorption can be observed. The distinction of this region suggests that the content of surface OH in CeC and CeT is higher than that in CeM. The band at 1 620 cm⁻¹ is assigned to the adsorption of H_2O[33]. On the basis of literatures[31,34-35], the bands around 1 555, 1 347, 1 142, 1 056, 913, 851 and 722 cm⁻¹ are representative of carbonate species. It should be noted that the bands around 1 555 and 1 347 cm⁻¹ are likely attributed to the carbonate species generated from the precipitant, since they are not observed in CeC and CeT, while the others are related to the carbonate species caused by the interaction of precipitates with atmospheric carbon dioxide[36]. It is obvious that the IR spectra of CeC and CeT are almost the same, indicating that they possess similar chemical structure, which is consistent with the TG-DTA results. The results further prove that, in the second

precipitation step of two-step precipitation method, the CO_3^{2-} is superseded by OH^- groups.

The XPS spectra for precipitates are shown in Fig.3. In the spectrum of Ce3d, six peaks are all present for the samples from different synthesis routes. According to the literature[37], all the peaks may be attributed to the diversified states of Ce^{4+}, indicating that Ce^{3+} ions are all oxidized by H_2O_2' in agreement with the previous report[23]. In the O1s of precipitates (Fig.4), the peak around 529.7 eV is assigned to the oxygen in the lattice[37], while the binding energy around 531.5 and 532.7 eV are related to the hydroxyl and C=O oxygen, respectively[38-39]. It is noted that, the 532.7 eV signal of CeM is much stronger than that of CeC and CeT, suggesting the existence of larger amount of carbonate species, which provides another evidence for the occurrence of the substitution of CO_3^{2-} by OH^-, in accordance with DTA-TG and IR results. The relative amounts of Ce, O and C are listed in Table 1. The amount of CeC and CeT is almost the same, implying that they possess the same chemical compositions, whereas the atom ratio is much different for CeM. The content of carbon in CeM is significantly higher than the other two samples due to the participation of carbonate during precipitation process. The amount of carbon cannot be evaluated accurately
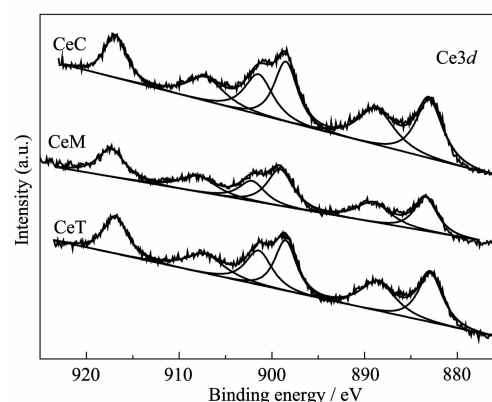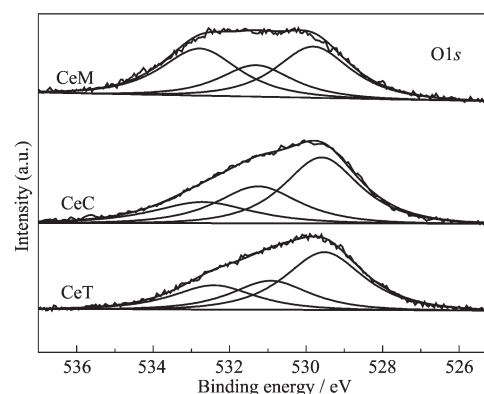

Fig.3　Ce3d XPS spectra for precipitates

Fig.4　O1s XPS spectra for precipitates

because the adventitious organic compounds generated from vacuum system are not easily excluded[23].

Table 1　Relative amount of Ce, O, and C, obtained from XPS spectra

| Precipitate	Ce / atom%	O / atom%	C / atom%
CeC	16.7	60.3	23.0
CeM	8.5	52.5	39.0
CeT	15.4	60.4	24.2

2.2　Textural properties of CeO₂ samples

The surface areas and pore volumes of CeO₂ samples calcined at various temperatures are shown in Fig.5. It can be seen that the CeO₂ samples prepared by the two-step precipitation method present larger surface area and pore volume than that produced by conventional precipitation method. A severe drop in surface area can be observed for conventionally prepared CeO₂ at different calcination temperatures, whereas the use of two-precipitation route effectively improves the thermal stability to 900 ℃, where a surface area of 25 m²·g⁻¹ and a pore volume of 0.11 cm³·g⁻¹ can still be obtained. To the best of our knowledge, the surface area and pore volume obtained in this work are the highest values reported for CeO₂ prepared by precipitation method and calcined at such a high temperature[11,17,31]. The CeO₂ samples calcined at 500 ℃ feature isothermals of type Ⅳ according to IUPAC definition, and the curves show a characteristic of cylindrical-ink-bottle-type pores (Fig.6a), through which the gas and thermal diffusion can proceed more easily than any other pore structure[40]. BJH pore size
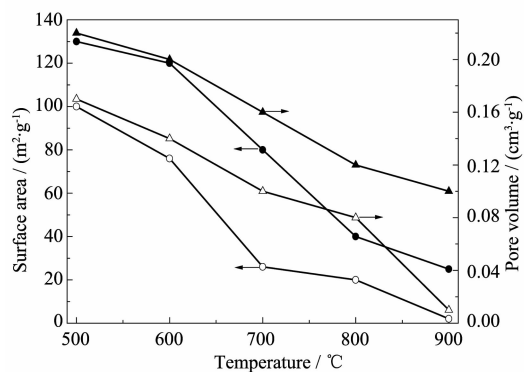
distribution of sample CeT calcined at 500 ℃ has a ○ and △ represent the surface area and pore volume of CeO₂ prepared by convention precipitation method; ● and ▲ represent the surface area and pore volume of CeO₂ obtained by two-step precipitation route

Fig.5　Textural properties vs calcination temperatures
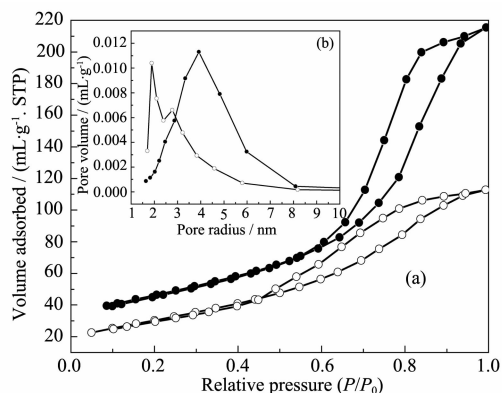
(○) CeO₂ prepared by convention precipitation method and (●) CeO₂ obtained by two-step precipitation route. The samples are calcined at 500 ℃

Fig.6　(a) N₂ adsorption-desorption isotherms of samples prepared by different methods; (b) the corresponding BJH pore size distribution curves

range of 2~8 nm, while for sample CeC, the value is 2~6 nm （Fig.6b）. Note also that, the peak position of CeC centers at around 2~3 nm, while for CeT, the value is larger （4.0 nm）, from which we can conclude that, through the novel two-step precipitation method, larger pores can be created. CeO₂-based material with larger pore size exhibits better thermal stability due to its long-range migration while sintering[29].

X-ray diffraction patterns indicate the presence of a single phase with the cubic fluorite structure typical of CeO₂, regardless of preparation routes (Fig.7). Crystallite sizes of the precipitates were calculated using （111) plane. The crystallite size of CeC is about
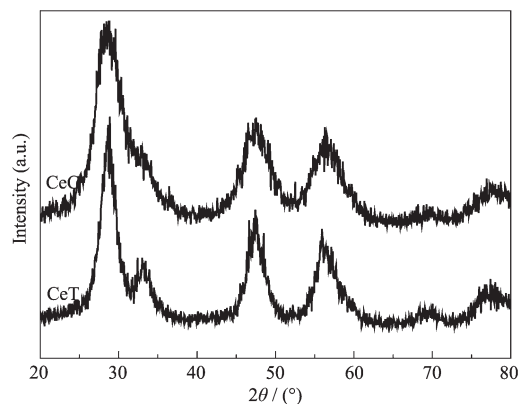

Fig.7　XRD patterns for precipitates

1.9 nm, which is smaller than that of CeT （3.8 nm）. In other words, although the chemical components of CeC and CeT are almost the same the crystal dimensions present a glaring discrepancy. With progressively increasing concentration of the reaction solutions, the mean magnitude for the individual crystals will decrease [41]. In the process of （1.1.1) precipitation, the OH⁻ with high concentration can attack Ce(Ⅳ) directly, resulting in crystals with smaller size. However, in the case of two-step precipitation method (1.1.3), crystallization of CeO₂ proceeds through gradual replacement of CO₃²⁻ by OH⁻, thus makes the crystallite size larger, which may facilitates the formation of CeO₂ with improved thermal resistance because coarser powders require a higher temperature to sinter[28].

TEM images of the precipitates are shown in Fig.8. It is apparent that the particles are approximately spherical and the grain size of CeT is larger than that of CeC. The results confirm the formation of CeO₂, indicating that the replacement of CO₃²⁻ by OH⁻ and the crystallization of CeO₂(OH)₂ have occurred. The results are in agreement with XRD outcomes, indicating that
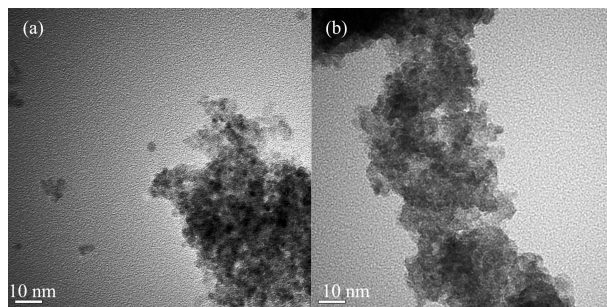
(a) CeC; (b) CeT

Fig.8　TEM of precipitates

the growth of CeO₂ is affected by the preparation route.

2.3　Reduction behavior of CeO₂ samples

　　A crucial requirement of CeO₂-based materials, especially when used in three-way catalyst for auto exhaust treatment, is their reduction behavior. Fig.9 displays the TPR profiles of the CeO₂ samples. The reduction of CeO₂ samples shows two peaks, the lower one is ascribed to the reduction of surface oxygen species, while the higher one corresponds to the contribution of bulk oxygen species [42]. The onset and the reduction peaks of CeT-t are lower than that of CeC-t, indicating that the former is more reducible, which is likely to be related to the disparity of surface areas [22]. Moreover, by comparing the integrated peak area of the TPR profiles, we can estimate that the oxygen storage capacity of CeT-t is larger than that of CeC-t [43].
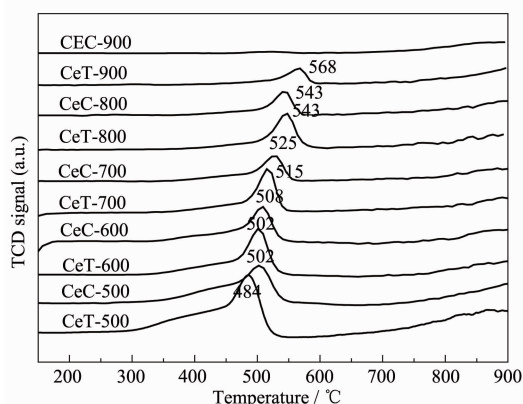

Fig.9　TPR profiles of CeO₂ samples

3　Conclusions

　　A two-step precipitation route was developed using ammonium carbonate and ammonia as precipitants successively. The formation mechanism of the CeO₂ precipitates was also investigated. The chemical compositions were the same for the precipitates prepared by the two-step method and conventional precipitation route employing ammonia as reactant. However, the crystallite size and the pore size of the as-prepared CeO₂ from two-step procedure are larger, which facilitate producing CeO₂ with improved thermal stability, textural properties and reduction behavior. After calcination at 900 ℃ for 3 h, the surface area and pore volume are 25 m²·g⁻¹ and 0.11 cm³·g⁻¹, respectively, which is the highest reported for CeO₂ at the temperature investigated.

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