0, 1, 3 维 CeO₂ 的可控制备及 CuO/CeO₂ 催化剂上 CO 氧化反应

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摘要: 以水、乙醇和乙二醇为溶剂, 采用溶剂热法可控制备了 0, 1, 3 维 CeO₂。结果表明, 0 维 CeO₂ 由 0.2~0.5 μm 纳米粒子组成; 1 维 CeO₂ 是直径为 25~30 μm, 长约 500 μm 的六方棒; 松针型的 3 维 CeO₂ 是由以纳米粒子为单元构成的直径为 1~5 μm, 长约 50 μm 的光滑棒组成, 其比表面积高达 234 m²/g。将 0, 1, 3 维 CeO₂ 负载的 CuO 催化剂用于 CO 氧化反应中, 发现以 1 维和 3 维 CeO₂ 为载体时, CuO 催化剂具有较大的比表面积和较强的表面还原性, 因而表现出较高的催化活性。

关键词: 氧化铈; 氧化铜; 一氧化碳; 氧化; 纳米结构; 拉曼光谱

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Synthesis of Zero, One, and Three Dimensional CeO₂ Particles and CO Oxidation over CuO/CeO₂

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Abstract: A method to synthesize zero, one, and three dimensional (0D, 1D, 3D) CeO₂ from single crystal cerium formate by a surfactant-free route using H₂O, ethanol and ethylene glycol as solvents is shown. 0D CeO₂ was composed of aggregated particles of 0.2–0.5 μm. 1D CeO₂ was hexagonal rods that were 25–30 μm in width and more than 500 μm in length. The pine needle shaped 3D CeO₂ was assembled from smooth rods of 1 to 5 μm diameter and up to 50 μm length that had CeO₂ nanoparticles as building units to give 3D micro/nanocomposite structures with a high BET surface area of 234 m²/g. Both 5 wt% CuO/1D CeO₂ and 5 wt% CuO/3D CeO₂ exhibited high catalytic activities for CO conversion due to the high BET surface area and the facile reducibility of surface CeO₂.

Key words: ceria; copper oxide; carbon monoxide; oxidation; nanostructure; Raman spectroscopy

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Ceria is an important oxide support used in catalytic ap- plications in which oxidation-reduction processes are in-

volved. The importance of CeO₂ in catalysis is due to its remarkable redox property and oxygen storage capability (OSC). These features are believed to be due to the easy creation and diffusion of oxygen vacancies, especially on the ceria surface. Many works have been performed to understand the function of the oxygen vacancies and to improve the reducibility of CeO₂ materials [1,2]. Ceria made in nanostructure form is promising as a catalytic material because it shows interesting properties related to its oxygen vacancy and reducibility resulting from its morphology and nanostructure, including its size, shape, surface/volume ratio, and crystal planes [3–5].

In the past few years, many efforts have been made to prepare multidimensional cerium oxide with different morphologies [6–9]. Several reports on the relationship between the catalytic activity and structure of the multidimensional CeO₂ particles have been published [10–12]. Mai et al. [13] synthesized ceria of various shapes using a hydrothermal method, and observed that ceria nanorods showed a higher OSC than the nanoparticles. Zhou and co-workers [14] converted CeO₂ nanorods into nanotubes in an H₂O₂ solution assisted by ultrasonication, and showed that the nanotubes were easily reducible, and that this was due to the higher reactivity of the CeO₂ surface (100) over that of the more common (111) surface. Recently, Pan et al. [15] reported the catalytic activity of two dimensional (2D) CeO₂ nanoplates. An enhanced catalytic activity for CO oxidation was found with CeO₂ nanoplates compared with CeO₂ nanotubes and nanorods. Zhong et al. [16] and Sun et al. [17] synthesized three dimensional (3D) flowerlike ceria micro/nanocomposite structures that showed a much better performance for CO removal and ethanol stream reforming than commercial ceria particles when used as pure ceria as a support. The reason could be because of their highly porous structure and high specific surface area. It was suggested that these structural characteristics of CeO₂ were likely to affect their performance in catalysis. However, most of the preparation processes were complex and a surfactant was used. The relationship between reducibility and morphology was not completely clarified.

Here, we report a method to synthesize zero, one, and three dimensional (0D, 1D, and 3D) structured CeO₂ using a solvothermal method without a surfactant. The formation process of CeO₂ with different morphologies is discussed. The 0D, 1D, and 3D CeO₂ obtained had surface areas of 97, 223, and 234 m²/g, respectively. Their plentiful oxygen

vacancies were shown by Raman spectroscopy. The reducibility was studied by temperature-programmed reduction (TPR). It was found that enhanced surface reducibility and high BET surface area led to a high catalytic activity for CO oxidation.

1 Experimental

1.1 Preparation of the materials

CeO₂ with 0D, 1D, and 3D morphologies were prepared in a 30 ml teflon-lined stainless steel autoclave by a solvothermal process using a water, ethanol, and ethylene glycol solution as solvent (listed in Table 1). The resulting solid was washed with absolute ethanol, dried in air, and calcined at 450 °C for 3 h. The Cu/CeO₂ catalysts were prepared by adding CO(NH)₂ to a solution containing suspended Cu(NO₃)₂ and CeO₂ powders. The resulting solid was washed, dried, and calcined at 450 °C for 3 h.

1.2 Characterization

The specific surface areas of the samples were obtained using N₂ at –196 °C with a Sorptometer Coulter SA 3100. Scanning electron microscopy (SEM) investigations were carried out using a KYKY-1000B apparatus. X-ray powder diffraction (XRD) patterns were recorded on a Siemens D-5000 powder diffractometer using nickel filtered Cu K_α radiation ($\lambda = 0.15406$ nm). Visible Raman spectra were recorded on a Jobin-Yvon U1000 apparatus with a 532 nm single frequency laser. Temperature-programmed reduction (TPR) was performed by heating the samples (30 mg) at 10 °C/min from 25 to 900 °C in a 5% H₂-95% N₂ mixture flowing at 40 ml/min.

1.3 Catalytic activity measurements

The catalytic activity for CO oxidation was evaluated in a fixed bed quartz tubular reactor using 50 mg of catalysts (40–60 mesh). The feed gas consisted of 0.25% CO and 0.50% O₂ in N₂ with a total flow rate of 80 ml/min, which corresponded to a space velocity (SV) of 96000 ml/g. A Hayerry D column (5 m) and a 13 X column (2 m) were used to separate the gaseous products, CO₂, CO, O₂, and N₂, which were analyzed using an Agilent 6890 gas chromatograph equipped with a TCD detector.

Table 1 Preparation conditions of the CeO₂ samples

Sample	Cerium precursor	H ₂ O (ml)	C ₂ H ₅ OH (ml)	C ₂ H ₆ O ₂ (ml)	Autoclaving temperature (°C)	Autoclaving time (h)
0D CeO ₂	Ce(NO ₃) ₃ ·6H ₂ O	0	10	10	220	24
1D CeO ₂	(NH ₄) ₂ Ce(NO ₃) ₆	5	5	10	150	24
3D CeO ₂	(NH ₄) ₂ Ce(NO ₃) ₆	0	10	10	130	120

2 Results and discussion

2.1 The structure of CeO₂ samples

Fig. 1(a) shows the XRD patterns of the samples before calcination. A crystalline product was formed in the 1D CeO₂ and 3D CeO₂ samples, which was shown to be a pure phase of hexagonal crystallized Ce(HCOO)₃ by the XRD data. The (101) and (401) peaks in the XRD patterns cannot be observed due to the needle crystalline orientation, which agreed with the XRD patterns shown in the literature (JCPDS 49-1245). The 0D CeO₂ sample showed different diffraction peaks compared with the 1D CeO₂ and 3D CeO₂ samples. All the broad and weak diffraction peaks were ascribed to cubic CeO₂.

Fig. 1. XRD patterns of the samples before calcination (a) and calcined at 450 °C for 3 h in air (b). (1) 0D CeO₂; (2) 1D CeO₂; (3) 3D CeO₂.

Figure 1(b) shows XRD patterns of the CeO₂ samples after calcination at 450 °C for 3 h in air. All the diffraction peaks were indexed to cubic CeO₂ with lattice constants in agreement with the values of JCPDS 34-394. The average particle size of the cerium oxide was calculated from the XRD patterns and the Scherrer equation to be less than 15 nm (Table 2). The cell parameters and BET surface areas are also listed in Table 2. The 0D CeO₂, 1D CeO₂, and 3D

CeO₂ samples showed large surface areas that were 97, 223, and 234 m²/g, respectively.

Table 2 Surface area, lattice parameter, and particle size

Sample	<i>A</i> _{BET} /(m ² /g)	Lattice parameter (nm)	Particle size (nm)
0D CeO ₂	97	0.5410	11.8
1D CeO ₂	223	0.5408	10.6
3D CeO ₂	234	0.5416	12.6

The formation of Ce(HCOO)₃ and CeO₂ can be summarized by the following reactions:

Ce(HCOO)₃ crystals were formed in the solution when C₂H₆O₂ was oxidized by O₂ with Ce³⁺/Ce⁴⁺ as catalyst (Ce³⁺ ions were oxidized by O₂ to form Ce⁴⁺, and C₂H₆O₂ was oxidized by Ce⁴⁺ ions to give HCOO⁻ and Ce³⁺). Reaction temperature, solution composition, and type of cerium salt were factors that influenced the formation of Ce(HCOO)₃ and CeO₂. A large amount of Ce⁴⁺ was necessary for the formation of the Ce(HCOO)₃ crystal, which was a key factor for the formation of CeO₂ with different morphologies. Instead of the Ce(HCOO)₃ crystal, CeO₂ formed as the 0D CeO₂ sample was due to that Ce³⁺ was used as cerium precursor and C₂H₆O₂ was not oxidized to Ce(HCOO)₃.

Figure 2 shows SEM images of the CeO₂ samples. 0D CeO₂ was composed of particles of 0.2–0.5 μm. Figure 2(b) exhibits the TEM image of the 1D CeO₂ hexagonal rods, which were 25–30 μm in width and more than 500 μm in length. A pine needle-like shape crystal was assembled from smooth rods in the 3D CeO₂ sample. The rods were 1 to 5 μm in diameter and up to 50 μm in length, and were grown from one center to form the pine needle-shaped crystals.

CeO₂ has the fluorite structure and has a Raman active triply degenerate F_{2g} mode at 465 cm⁻¹ [18]. However, in the spectra from our CeO₂ samples shown in Fig. 3, this mode was centered at 450 cm⁻¹, which showed more red shift than that reported by other authors for nano-ceria samples [19]. This shift may imply that changes in the lattice parameter with particle size had occurred. It was previously reported that a change of the particle size of CeO₂ from 5 μm to 6 nm led to a shifted peak position of about 10 cm⁻¹ [20]. Another reason of the shift could be the presence of CeO₂ defects, corresponding to non-stoichiometric CeO_{2-δ} [21]. Besides the main band at 450 cm⁻¹ in the Raman spectra, there were a weak peak at 550–600 cm⁻¹ and a weaker peak at 1100–1200 cm⁻¹ (relative to the 465 cm⁻¹), which were attributed to the second order Raman mode centered at O²⁻ vacancies [22]. The appearance of this mode was due to the increasing concentration of oxygen vacancies and the presence of Ce³⁺ sites [23].

Fig. 2. SEM and TEM images of the CeO₂ samples.

Fig. 3. Raman spectra of CeO₂ excited by a 532 nm laser.

2.2 Reducibility and catalytic activity of CeO₂ and 5% CuO/CeO₂

It is widely accepted that the migration of oxygen in ceria and ceria-based materials takes place via a vacancy hopping

mechanism. Oxygen vacancies were shown to be responsible for the migration of oxygen [24]. When the diffusion of anions is sufficiently fast, a continuous supply of oxygen from the bulk to the surface would guarantee an enhanced reducibility. In redox catalysis, the role of ceria is usually to act as an oxygen transfer component. The reducibility is an important characteristic that determines the catalytic properties of the catalyst. The H₂-TPR was used to measure this characteristic.

Figure 4 shows the H₂-TPR profiles of CeO₂ and 5% CuO/CeO₂. As shown in Fig. 4(a), the H₂-TPR profiles contain two reduction peaks, which were due to surface reduction at 400–650 °C and bulk reduction at higher than 700 °C [25,26]. The low temperature peak (below 650 °C) was of particular interest since the oxygen contributing to it would be readily available during a catalytic operation. Normally, surface reduction is much less than bulk reduction [27], but the surface reduction of all our CeO₂ samples in Fig. 4(a) was greatly enhanced as compared with bulk CeO₂. The larger area of this peak for these CeO₂ samples revealed that there were more oxygen available on the surface. The quantitative evaluation revealed that the amount of hydrogen consumed by surface ceria was much higher than that by

Fig. 4. TPR profiles of CeO₂ (a) and 5%CuO/CeO₂ (b)

Fig. 5. Catalytic activity of CeO₂ (a) and 5%CuO/CeO₂ (b) for CO oxidation.

bulk CeO₂ for 3D CeO₂. In addition, a new peak at 180 °C was ascribed to the reduction of adsorbed species on the surface of 3D CeO₂, which could be adsorbed oxygen or OH groups that can be reduced at low temperature. These observations indicated that the increased oxygen vacancies in 3D CeO₂ increased the active gas oxygen capacity and reducibility of surface CeO₂. We believe these properties exhibited by this novel material should allow 3D CeO₂ to find wide applications in catalytic fields.

Figure 4(b) shows the H₂-TPR profiles of 5%CuO/CeO₂. The peak at 200 °C for the 5%CuO/CeO₂ samples was ascribed to the reduction of Cu species. The peaks at 520 and 780 °C for both samples were ascribed to the reduction of surface and bulk oxygen of CeO₂, respectively. The surface reduction of 0D CeO₂ was much decreased and bulk reduction showed an obvious increase for the 5%CuO/0D CeO₂ sample. The loading of CuO on the surface of CeO₂ also reduced the amount of surface oxygen reduced for 5%CuO/1D CeO₂ and 5%CuO/3D CeO₂, but the amount of surface reduction was higher than that of 5%CuO/0D CeO₂.

The catalytic activity for CO oxidation as a function of temperature is presented in Fig. 5. A low reaction temperature was found with 1D CeO₂ or 3D CeO₂ used as the support with 5% CuO loading. 100% CO conversion was observed at the low temperature of 100 °C. The catalytic activities were also compared in terms of the temperatures (T_{50} , T_{90}) where 50% and 90% CO were converted to CO₂. The T_{50} and T_{90} in CO oxidation reaction were 317 and 380 °C for 3D CeO₂, which were about 10 °C lower than those of 1D CeO₂ and 0D CeO₂. The 5%CuO/1D CeO₂ catalyst showed a similar catalytic activity to 5%CuO/3D CeO₂, which was higher than that of 5%CuO/0D CeO₂.

It is generally accepted that the mechanism of CO catalytic oxidation is a redox Mars-van Krevelen reaction in which CO reacts with the catalyst surface to form an oxygen

vacancy, which is then replenished by gas phase oxygen, to give the cycle of the formation and desorption of CO₂ [28]. In a CuO/CeO₂ catalyst, it is commonly believed that the finely dispersed CuO is the active phase for CO oxidation [29,30]. The high surface area of the support aided the formation of finely dispersed CuO. The higher catalytic activity of 5%CuO/1D CeO₂ and 5%CuO/3D CeO₂ was explained by that their larger BET surface areas gave more active catalytic sites for CO oxidation. The high oxygen vacancy concentration in this system facilitated the activation and transport of active oxygen species. The enhanced reducibility of surface oxygen was also crucial for the excellent catalytic activity observed.

3 Conclusions

Different dimensionally structured ceria nanostructures were prepared by a simple solvothermal method. As compared with 0D CeO₂, 1D CeO₂, and 3D CeO₂ had high BET surface areas of 223 and 234 m²/g, respectively. The surface reducibility of 1D CeO₂ or 3D CeO₂ was enhanced by oxygen vacancies, which facilitated the activation and transport of active oxygen species. Both 5%CuO/1D CeO₂ and 5%CuO/3D CeO₂ gave higher activities for CO catalytic oxidation than 5%CuO/0D CeO₂.

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