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Redox properties and CO₂ capture ability of CeO₂ prepared by a glycol solvothermal method

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ABSTRACT

CeO₂ nanocrystals with plentiful oxygen vacancies were synthesized by a glycol solvothermal method (CeO₂-GST) using the strong reducibility of glycol. For comparison, CeO₂ nanorods (CeO₂-nanorods) and CeO₂ nanoparticles (CeO₂-CA) were also prepared. The samples were characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, H₂ reduction-O₂ oxidation cycle experiments and in situ CO₂ infrared spectroscopy. The CeO₂-GST sample exposed mainly (111) facets with abundant Ce³⁺ ions on its surface, and it gave excellent reversible redox behavior and high oxygen storage capacity. After seven H₂ reduction-O₂ oxidation cycles, the oxygen storage capacity became stable. The CeO₂-GST sample also had a high CO₂ adsorption capacity of 149 μmol/g at 50 °C by forming bidentate and bridge carbonates on the CeO₂ surface. These carbonate species were less stable than the unidentate carbonate, bicarbonate and formate species, thus adsorbed CO₂ was released easily. On reduced CeO₂ nanorod, CO₂ formed the stable unidentate carbonate and formate species, which is unfavorable for the release of adsorbed CO₂.

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1. Introduction

CeO₂ and CeO₂-based oxides have been studied intensively as catalyst, metal support and promoter [1–5]. CeO₂ is widely used in three-way catalysts because of its unique oxygen storage capacity (OSC). Depending on the nature and temperature of the pretreatment, CeO₂ has versatile acid-base properties and can be applied in many organic reactions [6,7]. Many synthesis approaches have been employed in the synthesis of ceria-based nano-materials with well-defined crystal planes. As early as 1988, Hsu et al. [8] reported the preparation of polycrystalline CeO₂ spheres with a uniform size by forced hydroly-

sis of cerium salt in sulfuric acid followed by aging at a critical temperature. Mai et al. [9] reported the synthesis of shape-selective CeO₂ nanorods, nanopolyhedrals and nanocubes by an alkali hydrothermal method. In 2011, it was reported for the first time that CeO₂ nanosheets exposing (110) facets were successfully prepared by a facile hydrothermal method [10].

Density functional theory (DFT) studies have shown that the (111) facet of CeO₂ has the lowest surface energy, followed by the (110) facet, and the (100) facet has the highest surface energy. Less energy would be required to form oxygen vacancies on a facet with a higher surface energy [11–14]. Thus the selective exposure of high energy facets would facilitate the for-

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mation of oxygen vacancies, which in turn would improve the OSC of ceria. In addition, oxygen vacancy clusters promotes the reducibility and activity of ceria nanorods [15]. Clusters such as linear surface oxygen vacancies had proved helpful for the migration of oxygen from the bulk to the surface, and thus would make CeO₂ more reducible [16].

Nowadays, much attention is paid to global warming, and it is desirable to design materials to store CO₂ or develop process to convert CO₂ into valuable chemicals. CO₂ can be activated by reduced CeO₂. One mechanism proposed for CO₂ activation is that CO₂ is reduced directly into CO on reduced CeO₂ [17,18]. However, Lykhach et al. [19,20] reported that CO₂ activation on reduced CeO₂ led to the rapid formation of a carbonate and surface carboxylates. A DFT study of CO₂ activation on reduced CeO₂ (110) also proved that CO₂ activation on reduced CeO₂ (110) proceeded with CO₂ adsorbed parallel to the surface by forming stable carbonate species [21]. Yang and coworkers reported that a Sm-doped CeO₂ nanomaterial showed excellent CO₂ capture ability. They attributed the CO₂ adsorption ability to the abundant oxygen vacancies of Sm-doped CeO₂ [22].

Glycol is a very useful organic solvent in metal and metal oxide preparation because of its strong reducibility. CeO₂ prepared in its presence would have lots of oxygen defects on the surface, which would improve its OSC and gas capture ability. Here, an improved CeO₂ nanomaterial was prepared by a glycol solvothermal method and its OSC property was studied. Its CO₂ storage property was explored by a CO₂ pulse technique and CO₂ in situ diffuse reflectance infrared spectroscopy (DRIFTS).

2. Experimental

2.1. Catalyst preparation

CeO₂ nanomaterials were prepared by three different methods with commercial reagents. Analytical grade Ce(NO₃)₃·6H₂O, NaOH, ethylene glycol and citric acid were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification.

For the preparation of CeO₂-GST, 5 mmol of Ce(NO₃)₃·6H₂O was added into 60 mL ethylene glycol with stirring for 20 min under ambient temperature. This was transferred into a 100 mL Teflon-lined stainless steel autoclave for crystallization at 180 °C for 24 h. The solid product was separated by centrifugation and washed with acetone three times and then dried at 50 °C overnight. This sample was marked as CeO₂-GST. In most cases, the sample was calcined at 600 °C for 3 h with a heating rate for 1 °C/min.

The CeO₂-nanorod was synthesized by a traditional hydrothermal method given in a previous report [9]. 5 mmol of Ce(NO₃)₃·6H₂O and 0.8 mol of NaOH were dissolved in 80 mL deionized water and stirred for 30 min at ambient temperature. The mixture was transferred into a Teflon-lined stainless steel autoclave for crystallization at 120 °C for 48 h. The product was filtered and washed with distilled water until it was neutral and then dried at 50 °C. This sample was denoted as CeO₂-nanorod. In most cases, the sample was also calcined at 600 °C for 3 h with a heating rate for 1 °C/min.

For CeO₂-CA, 5 mmol of Ce(NO₃)₃·6H₂O and 15 mmol of citric acid were dissolved in 80 mL deionized water. The solution was heated to 80 °C under stirring and kept for 12 hours at 80 °C in a closed environment to form a gel. After that, the gel was dried at 100 °C. The sample was calcined at 600 °C for 3 h with a heating rate for 1 °C/min and denoted as CeO₂-CA.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Focus diffractometer (Cu K α radiation, λ = 1.5406 Å) operated at 40 kV and 40 mA. BET specific surface areas were measured at -196 °C on a Quantachrome NOVA 4200e instrument. The sample was outgassed at 200 °C for 12 h before measurement. High resolution transmission electron microscopy (HR-TEM) images of the synthesized ceria were taken on a JEOL-2010 field emission transmission electron microscope. X-ray photoelectron spectroscopy (XPS) spectra were measured using a Thermo ESCA LAB-250 spectrometer with monochromatic Al K α radiation. The binding energies were calibrated internally by the carbon deposit C 1s binding energy (BE) at 284.8 eV. The deconvolution of the XPS spectra used Gaussian functions.

H₂ temperature-programmed reduction (H₂-TPR) of the CeO₂ samples (100 mg) was investigated by heating a CeO₂ sample in a 5% H₂/N₂ flow (40 mL/min) at the heating rate of 10 °C/min from 30 to 600 °C. The hydrogen consumption was monitored by a thermal conductivity detector (TCD) using a zeolite for water adsorption. After the H₂-TPR analysis, the same sample was cooled to 100 °C, and the gas flow was switched to 3% O₂/He and the remaining H₂/N₂ was purged for 10 min. Then, the sample was re-oxidized by the O₂/He mixture gas at 500 °C for 2 h and cooled to ambient temperature. Afterwards, the gas was switched to the H₂/N₂ flow again, which completed one H₂ reduction-O₂ oxidation cycle. Several cycles were repeated.

CO pulse adsorption was investigated on Auto Chem II 2920 Micrometrics instrument using a mass spectrometer (MS) to detect the gas product. For each of the three samples, 50 mg of CeO₂ was placed at the bottom of a U-shaped quartz tube which was first pretreated in an 5% O₂/He flow (purity 99.999%, 30 mL/min) at 400 °C for 30 min. Then the sample was flushed with pure He. When the baseline was stable, the CO pulse experiment was carried out using 5% CO/He (30 mL/min) as the pulsed gas.

CO₂ pulse experiments were also carried out on the Auto Chem II 2920 Micrometrics instrument using both MS and TCD as detectors. For each of the three samples, 25 mg of CeO₂ was first pre-reduced by 10% H₂/Ar flow (50 mL/min) at 600 °C for 30 min. Then the sample was cooled to 50 °C and flushed with pure He. After the baseline was stable, the CO₂ pulse experiment was conducted using 5% CO₂/He (30 mL/min) as the pulsed gas.

CO₂ in situ DRIFTS was performed using a Thermo Nicolet Nexus 670 spectrometer equipped with a MCT detector and a high temperature reaction chamber with ZnSe windows. Prior to each CO₂ adsorption experiment, ceria was first pretreated

with 10% H_2/N_2 (50 mL/min) at 500 °C for 30 min, cooled down to 300 °C, and then finally flushed with He (80 mL/min) for 30 min. After that, the sample was cooled to 50 °C and the background spectra were recorded in flowing He for the subtraction from the sample spectrum for each measurement. The CO_2 adsorption experiment was conducted at 50 °C using 5% CO_2/He (80 mL/min). As soon as CO_2 was flowed into the sample cell, the spectrum was collected in the range of 4000–650 cm^{-1} by accumulating 64 scans at a 4 cm^{-1} resolution, DRIFTS spectra were recorded every 2 min. After the sample was exposed to CO_2 flow for 20 min, He flow was switched in to flush for 20 min. During the He flushing, spectra were also collected every two minutes.

3. Results and discussion

3.1. XRD, BET, and HR-TEM results

Figure 1 shows the XRD patterns of the calcined ceria prepared by the three different methods. CeO_2 -GST, CeO_2 -nanorod, and CeO_2 -CA were all in the pure cubic phase (fluorite structure, JCPDS 34-0394, space group $\text{Fm}\bar{3}\text{m}$). The BET surface areas of CeO_2 -GST, CeO_2 -nanorod, and CeO_2 -CA were 79.0, 78.0, and 49.0 m^2/g , respectively.

Figure 2 shows the HR-TEM images of the calcined ceria samples prepared by the different methods. For the sample prepared by the glycol solvothermal method (Fig. 2(a) and (b)), a hexahedral morphology was found for most of the CeO_2 particles. The particle size was uniformly distributed at 10–15 nm and the particle was mainly enclosed by {111} facets. The morphology of CeO_2 was not totally in accordance with that in Liang's report, where it was almost sphere-like and could be tuned to be cubic by adding some water into the original solution [23]. In our experiment, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved directly in glycol and no water was added. The morphology of CeO_2 -GST would be affected and it finally formed the hexahedral shape. The CeO_2 -nanorods (Fig. 2(c) and (d)) showed a rod-like shape (20 nm across, 60–300 nm long) with a preferential growth direction along the [110] direction, which exposed {100} facets. The CeO_2 -CA prepared by the sol-gel method

Fig. 1. XRD patterns of the CeO_2 samples after calcination. (1) CeO_2 -GST; (2) CeO_2 -nanorod; (3) CeO_2 -CA.

Fig. 2. TEM and HR-TEM images of CeO_2 -GST (a, b), CeO_2 -nanorod (c, d), and CeO_2 -CA (e, f). All the samples were calcined at 600 °C.

od (see Fig. 2 (e) and (f)) showed an irregular morphology and exposed {111} facets, with particle sizes that ranged from 5 to 20 nm.

3.2. XPS results

XPS was conducted to investigate the surface oxidation state of CeO_2 -GST before and after calcination. The CeO_2 -nanorod and CeO_2 -CA samples were also tested for comparison. As presented in Fig. 3, the Ce 3d spectra were composed of eight peaks corresponding to four pairs of spin-orbit doublets. According to a work reported previously [24–27], the Ce^{4+} spectrum was labelled with v, v', v''' and u, u'', u''', which were the $3d_{5/2}$ and $3d_{3/2}$ photoelectron peaks for $4f_7/2$, $4f_5/2$, and $4f_0$ occupation, respectively; v' and u' represented the lower binding energy peaks of the $3d_{5/2}$ and $3d_{3/2}$ electrons for the $4f_1/4f_2$ configuration in Ce^{3+} . The peaks marked as u (900.6–901.0 eV), u'' (907.5–907.7 eV), and u''' (916.6–916.9 eV) were from Ce^{4+} $3d_{3/2}$, while the peaks labelled as v (882.2–882.6 eV), v'' (889.1–889.3 eV), and v''' (898.2–898.5 eV) were from Ce^{4+} $3d_{5/2}$. The couples corresponding to one of the two possible electron configuration of the final state of the Ce^{3+} species were labelled as u' (903.5–904.2 eV) and v' (885.1–885.8 eV). The proportion of Ce^{3+} cation ratio is summarized in Table 1, which was calculated using the equation in reference [24].

Fig. 3. XPS spectra of CeO₂. (a) uncalcined CeO₂-GST; (b) calcined CeO₂-GST; (c) calcined CeO₂-nanorod; and (d) calcined CeO₂-CA.

From the XPS results, uncalcined CeO₂-GST showed the largest Ce³⁺ concentration of 63% (Table 1). The relative intensity of u' and v' attributed to Ce³⁺ was much higher than with the other samples and the u''' peak for Ce⁴⁺ could be barely seen. After calcination, surface Ce³⁺ was still preserved and present as 11.2% of the surface cations. The intensity of the u' and v' (Fig. 3(b) peaks decreased and the u''' peak attributed to Ce⁴⁺ increased correspondingly. For the three samples (Fig. 3(c) and (d)), the CeO₂-nanorod showed the lowest surface Ce³⁺ ratio of 5% and CeO₂-CA, which could be reduced by the re-

ducing gas generated in the decomposition of citric acid, showed the highest surface Ce³⁺ ratio of 14.6%. CeO₂-GST contained more Ce³⁺ than the sample from the traditional hydrothermal process because of the reduction of glycol by the valence change Ce⁴⁺ → Ce³⁺ [28,29]. This in turn indicated that there were more oxygen vacancies on the surface of CeO₂-GST than on the CeO₂-nanorod.

3.3. H₂ reduction-O₂ oxidation and CO pulse results

The H₂ reduction-O₂ oxidation cycle experiment was designed to investigate the reversible redox behavior of the CeO₂ samples. The oxygen release property of the samples was qualitatively analyzed by the CO pulse method using a MS as detector.

Figure 4 displayed the H₂ reduction-O₂ oxidation cycles of the three samples. The H₂ consumptions for all three samples are listed in Table 2. For the first cycle, the CeO₂-nanorod displayed the highest H₂ consumption (470 μmol/g), followed by CeO₂-GST (380 μmol/g) and CeO₂-CA (369 μmol/g). After that, the H₂ uptake for all three samples decreased. CeO₂-CA showed

Table 1

Ce³⁺ ratio and oxygen release rate *k* for CeO₂ samples prepared by the different methods.

Sample	Ce ³⁺ a (%)	<i>k</i> b
CeO ₂ -GST (uncalcined)	63.0	—
CeO ₂ -GST (calcined)	11.2	8.04E-11
CeO ₂ -nanorod	5.0	1.64E-11
CeO ₂ -CA	14.6	7.41E-11

^aThe Ce³⁺ ratio was calculated using the equation in the experimental section of Ref. [24]: Ce³⁺ = (v' + u')/(u + u' + u'' + u''' + v + v' + v'' + v''').

^b*k* represented the intercept of the CeO₂ samples in the CO pulse measurement (Fig. 7).

Fig. 4. H₂ reduction-O₂ oxidation cycles for the CeO₂ nanomaterials. (a) CeO₂-GST; (b) CeO₂-nanorod; (c) CeO₂-CA.

Table 2H₂ consumption of CeO₂-GST, CeO₂-nanorod, and CeO₂-CA.

Sample	Cycle	H ₂ consumption (μmol/g)
CeO ₂ -GST*	1	380
	2	266
	3	240
	4	215
	5	200
CeO ₂ -nanorod	1	470
	2	277
	3	257
	4	243
	5	224
CeO ₂ -CA	1	369
	2	130
	3	118

*The 6th–10th cycle H₂ consumptions for CeO₂-GST were 190, 184, 180, 180, and 175 μmol/g, respectively.

the weakest ability for oxygen re-storage and the H₂ uptake decreased from 369 to 118 μmol/g in just three cycles. The H₂ consumption of CeO₂-nanorod and CeO₂-GST were similar from the second cycle. However, the rod-like structure was broken after five cycles (Fig. 5(a) and (b)), while CeO₂-GST still remained intact even after cycling 10 times (Fig. 5(c) and (d)). The BET measurement showed that after the cycling, the surface area of the nanorod decreased from 78 to 6 m²/g, which was in agreement with the HR-TEM results. It should be pointed out that CeO₂-GST presented the most stable reversible redox ability of the three samples. The oxygen re-storage activity began to be constant after the sixth cycle (Fig. 4(a) and Table 2). The oxygen vacancies would favor the migration of oxygen and thus continuously supply oxygen from the bulk to the surface, which in turn stabilized the H₂ uptake capacity of

CeO₂-GST during the cycling. In addition, the glycol solvothermal condition improved structural stability of CeO₂-GST, and the morphology was preserved after 10 cycles.

Figure 6 shows the MS signal of the CO pulse experiments for the different CeO₂ samples at 400 °C. Each test with CO pulses lasted 16 pulses. It was seen that the CO peak for all of the three samples showed a linear growth in the first 10 pulses. After 13 CO pulses, the CO peak intensity showed no more growth for all the three samples. The integration of the peak areas represented the remaining CO amount. A linear relationship between the peak area and pulse number was obtained by fitting (Fig. 7). The intercept *k* is relevant to the oxygen release rate in our experiment and a larger value of *k* corresponded to a lower oxygen release rate. The *k* values of the CeO₂ samples are shown in Table 1. The linear correlation for *k* is displayed in Fig. 7. The CeO₂-nanorod exhibited the highest oxygen release activity, followed by the CeO₂-CA and CeO₂-GST.

According to first principle studies, the exposure of the more reactive (100) and (110) surfaces facilitate the formation of oxygen vacancies on the CeO₂ surface [24–26]. This was verified by our results that the CeO₂-nanorod had the highest oxygen release ability and H₂ consumption (470 μmol/g) due to the exposure of more reactive (100) facets. Both CeO₂-GST and CeO₂-CA mainly exposed the most stable (111) facet (Fig. 2(a) and (c)). By analyzing the other two samples, it was found that the release rate for CeO₂-GST was smaller than that of CeO₂-CA, as was the surface Ce³⁺. Thus it can be speculated that the surface defects generated by the formation of Ce³⁺ on the CeO₂ surface contributed to the OSC performance. A similar experiment conducted by Liu and co-workers made the same conclusion [15]. Thus, it can be deduced that the controlled synthesis of a CeO₂ nanomaterial that exposed abundant vacancies would improve the oxygen release ability, thus enhancing the catalytic activity of CeO₂.

3.4. CO₂ capture measurement

Generally, CO₂ capture is measured using an amine solvent, a membranes, or an ionic liquid [30,31]. The biggest challenge for all traditional CO₂ adsorption methods is the high regeneration energy for the adsorbent and high capital cost. Since CeO₂

Fig. 5. HR-TEM images of CeO₂ after H₂ reduction–O₂ oxidation for several cycles. (a, b) CeO₂-nanorod (5 times); (c, d) CeO₂-GST (10 times).

Fig. 6. MS signal of CO pulses from different CeO₂ samples. (1) CeO₂-GST; (2) CeO₂-nanorod; (3) CeO₂-CA.

Fig. 7. Integrated peak area versus pulse number for CeO₂-GST (a), CeO₂-nanorod (b), and CeO₂-CA (c). The intercept k was based on the plot of 10 CO pulse peak areas versus pulse number. In ten pulses, the peak areas showed a linear growth for all the three samples. Thus the k value corresponded to the oxygen release rate of each sample. The value of k was 8.03×10^{-11} , 7.41×10^{-11} , and 1.65×10^{-11} for CeO₂-GST, CeO₂-CA, and CeO₂-nanorod, respectively. A larger value of k corresponded to a slower oxygen release rate.

is a Lewis base, it is thermodynamically desirable for CO₂ adsorption [30,32]. In addition, CeO₂ with abundant exposed oxygen vacancies is a potent surface for gas adsorption [33]. In this section, the CO₂ capture ability of the CeO₂ samples is reported. The CO₂ adsorption state was also investigated by CO₂ in situ DRIFTS.

To test the CO₂ capture ability of the CeO₂ samples at 50 °C, a CO₂ pulse method was designed using TCD and MS to detect the products. It was found that no CO product was generated at 50 °C except for a small signal of 28 fragment peaks generated by CO₂. Figure 8 shows the MS signal of CO₂. The amount of adsorbed CO₂ was calculated from the TCD signals. CeO₂-GST showed the highest CO₂ adsorption of 149 μmol/g and the CeO₂-nanorod and CeO₂-CA showed similar values, which were 86 and 90 μmol/g, respectively.

Prior to the CO₂ in situ DRIFTS measurement, the sample was pretreated under a flow of 10% H₂/N₂ (50 mL/min) for 120 min at 500 °C and then switched to pure helium flow for 30 min at 300 °C (80 mL/min). After that, the temperature was cooled down to 50 °C and the background spectrum was recorded at this temperature. Then a gas mixture of 5% CO₂/He (80 mL/min) was fed into the reactor chamber to flow through the sample and the spectra were recorded. The assignments for

the peaks were based on previous studies and listed in Table 3 [34–39].

Figure 9 shows the infrared spectra of CeO₂ samples at 50 °C. For CeO₂-GST, six distinct peaks at 856, 1021, 1217, 1289, 1397, and 1584 cm⁻¹ in the region 800–2000 cm⁻¹ were detected (shown in Fig. 9(a)) after CO₂ was introduced into the sample cell. The peak increased when the sample was treated with CO₂ for a longer time and all the peaks became constant after 20 min of CO₂ exposure (Fig. 9(a)), which was regarded as that the sample had reached its saturation for CO₂ adsorption. CeO₂-CA showed a similar behavior to CeO₂-GST except that all the peak intensities were weaker (Fig. 9(c)). The CeO₂-nanorod showed quite different peaks in comparison with the other two samples. The bands at 1214 and 1392 cm⁻¹ were much stronger and there were several new bands at 1458, 1542, and 1617 cm⁻¹ (Fig. 9(b)). The peaks observed on CeO₂-GST and CeO₂-CA at 856, 1028, 1289, and 1584 cm⁻¹ were assigned to the bidentate carbonate. The bands at 1612, 1392, and 1214 cm⁻¹ were assigned to bicarbonate, the bands at 1217 (1214) and 1397 (1392) cm⁻¹ were assigned to bridge carbonate, 1458 cm⁻¹ was assigned to unidentate carbonate, and 1542 cm⁻¹ was assigned to formate [35,36].

After the samples were flushed with pure He for 10 min, some changes were observed. The peak at 1217 cm⁻¹ (1214 cm⁻¹ for CeO₂-nanorod) almost disappeared for all three samples. This was attributed to the instability of the bridge carbonate on the CeO₂ surface and the adsorbed bridge carbonate was easily removed by the He flush [34]. For the CeO₂-nanorod,

Fig. 8. MS signal of the CO₂ pulses. Each CO₂ pulse experiment used 13 pulses. For (1) CeO₂-GST, the CO₂ adsorption took 11 pulses to reach saturation, for (2) the CeO₂-nanorod 8 pulses, and for (3) CeO₂-CA 9 pulses.

Table 3

Assignment of IR bands for CO₂ adsorption on reduced ceria at 50 °C.

Sample	Plane	Species	Wavenumber (cm ⁻¹)
CeO ₂ -GST	(111)	Bidentate carbonate	856, 1028, 1289, 1584
		Bridge carbonate	1217, 1396
CeO ₂ -nanorod	(100)	Bridge carbonate	1217, 1392
		Unidentate carbonate	856, 1348, 1458
		Bidentate carbonate	856, 1028, 1289, 1586 (1563)
		Formate	1542
CeO ₂ -CA	(111)	Bicarbonate	1612
		Bidentate carbonate	856, 1028, 1289, 1583
		Bridge carbonate	1214, 1397

Fig. 9. In situ CO_2 DRIFTS spectra of the CeO_2 samples at 50°C . (a) CeO_2 -GST; (b) CeO_2 -nanorod; (c) CeO_2 -CA. (1) He flush 10 min; (2) CO_2 adsorption 0 min; (3) CO_2 adsorption 5 min; (4) CO_2 adsorption 20 min.

the peak at 1584 cm^{-1} did not appear and there was a new peak at 1563 cm^{-1} (Fig. 9(b)), which indicated that the reduced CeO_2 was re-oxidized by CO_2 , making the highest wavenumber due to the $\nu(\text{OCO})$ mode of bidentate carbonate shift from 1584 cm^{-1} to 1563 cm^{-1} [36]. The peaks attributed to bicarbonate, unidentate carbonate and formate on nanorod were all preserved after helium flushing. It is worth noting that the intensity of the 1217 cm^{-1} peak on the nanorod was stronger than on the other two samples, which was due to the easier formation of bridge carbonate on the reduced (100) facet. For CeO_2 -GST, the band at 1584 cm^{-1} was changed slightly (Fig. 9(a)) and the peak at 1563 cm^{-1} was not found during the experiment. This indicated that there was no bicarbonate species on the surfaces of CeO_2 -GST and CeO_2 -CA.

From the stable species after the pure He gas flush, it was found that CO_2 was activated by CeO_2 -nanorod forming more stable species such as unidentate carbonate, bicarbonate and formate. Since there was no signal of CO detected in the MS signal and no adsorbed CO IR peak at $2000\text{--}2100\text{ cm}^{-1}$. It can be deduced that CO_2 re-oxidized the reduced CeO_2 -nanorod by forming stable carbonate species, which was in agreement with the DFT study on the reduced $\text{CeO}_2(110)$ facet [21]. Thus, the CeO_2 -nanorod would react CO_2 rather than capture it. The IR spectra also suggested that CO_2 was preferentially adsorbed on the reduced (111) facet in the form of the less stable bidentate carbonate. The differences in the band intensities between CeO_2 -GST and CeO_2 -CA were distinct, which was attributed to their different BET surface areas. Since the active site for CO_2 adsorption is Ce^{3+} , reduced $\text{CeO}_2(100)$ was so active that it would activate CO_2 by oxidizing Ce^{3+} into Ce^{4+} , which would limit CO_2 capture. It was considered that CeO_2 -GST was more efficient for CO_2 adsorption because of abundant oxygen vacancy clusters on its surface and the $\text{CeO}_2(111)$ facets also contributed to the CO_2 capture ability of CeO_2 -GST by stabilizing the bidentate carbonate species.

4. Conclusions

A CeO_2 -GST sample prepared by a glycol solvothermal method had abundant surface oxygen vacancy clusters and exhibited excellent reversible redox ability. The oxygen vacan-

cies generated in the solvothermal process were preserved even after calcination and they improved the reducibility of CeO_2 , thus providing a continuous oxygen supply from the bulk to the surface, which made this CeO_2 stable during H_2 -consumption in the H_2 reduction- O_2 oxidation cycles. In contrast, the CeO_2 -nanorod displayed rather poor reversible redox performance. Moreover, the CO_2 storage measurements with the reduced CeO_2 nanomaterials (CeO_2 -GST, CeO_2 -nanorod, CeO_2 -CA) showed that CeO_2 -GST had the highest CO_2 storage capacity ($149\text{ }\mu\text{mol/g}$) of the three samples. CO_2 adsorption on the CeO_2 nanomaterials was also different, which was mainly due to the exposure of different planes on the different samples. The bidentate carbonate was preferentially adsorbed on the reduced (111) facet, while the reduced (100) facet favored the stable bridge carbonate. CeO_2 with more vacancy clusters on the surface and with a larger BET surface area gave good CO_2 adsorption capacity and thus is an excellent material for CO_2 capture.

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Graphical Abstract

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Redox properties and CO₂ capture ability of CeO₂ prepared by a glycol solvothermal method

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CeO₂ nanocrystal that has abundant oxygen vacancies was prepared by an ethylene glycol solvothermal method, and shown to have excellent CO₂ capture ability.

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乙二醇溶剂热合成的CeO₂的可逆氧化还原性及CO₂捕获性能

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摘要: 利用乙二醇的还原性, 采用乙二醇溶剂热法制备了表面具有丰富氧空穴的CeO₂-GST纳米晶, 对其进行了X射线衍射、透射电镜、X射线光电子能谱、原位H₂还原-O₂氧化循环和CO₂原位红外漫反射表征, 并研究了其可逆氧化还原性及CO₂捕获性能。结果表明, 与CeO₂-nanorod和柠檬酸溶胶法合成的CeO₂-CA样品相比, CeO₂-GST纳米晶具有最好的可逆氧化还原性能和循环稳定性, 同时在50 °C下具有最好的CO₂吸附性能(149 μmol/g)。利用原位红外漫反射光谱研究了CO₂在还原CeO₂表面的吸附情况, 发现CO₂主要以双齿碳酸盐和桥连碳酸盐两种形式吸附在CeO₂表面, 其中桥连碳酸盐物种不稳定, He吹扫可脱附。此外, CO₂在CeO₂-nanorod上还会生成稳定的甲酸盐和单齿碳酸盐物种。

关键词: 氧化铈; 氧空穴; 可逆氧化还原性; 二氧化碳捕获; 二氧化碳原位红外漫反射

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1. 前言

作为稀土氧化物中重要的一员, CeO_2 以及Ce基复合氧化物已经被人们广泛研究^[1-5]. CeO_2 是一个很好的负载型催化剂载体, 同时也具有一些非常优异的催化性能. 例如, CeO_2 因其独特的储放氧性能而被用于汽车尾气净化器中的三效催化剂中; 通过预处理后的氧化铈表现出一定强度的碱性, 应用于催化有机缩合反应中^[6,7].

CeO_2 材料可通过多种成熟的方法合成. 早在1988年, Hsu等^[8]在强酸体系中水解铈盐的前驱体合成了尺寸十分均一的多晶 CeO_2 纳米球; Mai等^[9]在强碱性溶液中采用水热晶化的方式成功合成了 CeO_2 纳米棒、 CeO_2 纳米立方以及 CeO_2 多面体等不同形貌的 CeO_2 纳米材料; 最近有人报道, 通过简便的水热法即可成功制备暴露(110)活性面的 CeO_2 纳米片^[10].

人们通过密度泛函理论对 CeO_2 的低密勒指数晶面模拟计算发现, CeO_2 (111)面具有最低的表面能, 因而在(111)面上需要较高的能量才能形成氧空穴, 而(100)晶面具有最高的表面能, 有利于表面氧空穴的产生^[11-14]. 因此选择性地暴露出活性面将有利于 CeO_2 表面氧空穴的形成, 可提高其储放氧性能. 此外, 氧空穴簇能够增加 CeO_2 纳米棒的还原性和活性^[15], 这是因为氧空穴簇以线式结构存在于 CeO_2 表面, 促进体相氧向表面的迁移, 从而利于 CeO_2 的还原^[16].

如今温室效应越来越受到人们的关注. 通过设计优良的存储材料将温室气体 CO_2 存储或者通过一系列催化反应将其转化为高价值的精细化学品有利于减小 CO_2 温室气体的排放. 还原的 CeO_2 能够吸附 CO_2 , 其中有研究者认为 CO_2 在吸附过程中被活化生成CO^[17,18]; Lykhach等^[19,20]认为 CO_2 在 CeO_2 表面快速生成了碳酸盐物种而不会直接生成CO. 通过还原 CeO_2 (110)晶面的 CO_2 吸附理论计算结果证明, CO_2 在 CeO_2 表面是以碳酸盐形式吸附的^[21]. 最近, 研究发现Sm掺杂的 CeO_2 纳米材料在50 °C下具有非常优异的 CO_2 吸附性能, 表面丰富的氧空穴有利于 CO_2 的吸附^[22].

乙二醇具有很好的还原性能, 常被用于金属单质和金属氧化物的制备过程中. 在乙二醇溶剂热条件下合成 CeO_2 纳米材料, 有望使 CeO_2 表面暴露出更多的氧空穴, 从而能够提高其可逆氧化还原性、储放氧性能和 CO_2 的捕获能力. 本文采用乙二醇溶剂热法制备了 CeO_2 -GST纳米材料, 并测试了其可逆氧化还原性、储放氧性能及

CO_2 捕获性能. 此外还通过 CO_2 原位红外漫反射(DRIFTS)实验进一步研究了 CO_2 在 CeO_2 表面的吸附状态.

2. 实验部分

2.1. CeO_2 的制备

分析纯的 $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, NaOH, 乙二醇和柠檬酸从国药集团化学试剂有限公司购买, 所有试剂在使用前均未经过进一步纯化.

采用三种不同的方法制备 CeO_2 材料.

量取60 mL的乙二醇于聚四氟乙烯内衬中, 在搅拌条件下, 加入5 mmol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 继续搅拌20 min. 在 $\text{Ce}(\text{NO}_3)_3$ 全部溶解后, 将聚四氟内衬转移到晶化釜内, 180 °C晶化24 h. 反应结束后, 离心, 并用丙酮洗涤样品数次, 50 °C干燥过夜. 600 °C焙烧3 h, 升温速率1 °C/min. 所得样品标记为 CeO_2 -GST.

将5 mmol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 和0.8 mol的NaOH分别溶解在80 mL去离子水中, 然后在搅拌条件下, 将NaOH水溶液逐滴加入到硝酸铈溶液中, 滴完后继续搅拌30 min. 再转移到水热晶化釜中, 拧紧, 120 °C晶化48 h. 反应结束后取出晶化釜, 过滤, 并用去离子水多次洗涤至中性, 50 °C烘箱中干燥过夜. 600 °C焙烧3 h, 升温速率为1 °C/min. 所得样品标记为 CeO_2 -nanorod.

称取5 mmol $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 和15 mmol柠檬酸溶解在80 mL去离子水中, 将所得混合溶液转移到80 °C水浴中, 静置12 h使其成胶, 并陈化过夜. 之后把所得到的溶胶放入100 °C的烘箱中, 烘干剩余水分. 将所得淡黄色片状干胶研碎, 600 °C焙烧3 h, 升温速率为1 °C/min. 得到的样品标记为 CeO_2 -CA.

2.2. CeO_2 的表征

样品的晶体结构以及有关的晶胞参数测试均使用Bruker D8 FOCUS X射线衍射(XRD)仪. 仪器参数为: Cu靶 K_α 射线($\lambda = 1.5406 \text{ \AA}$), Ni单色器, 管电压为40 kV, 管电流为40 mA. 样品的比表面积采用Quantachrome NOVA 4200e型吸附仪进行分析, 实验前样品于200 °C脱气12 h. 样品的形貌以及晶格条纹采用日本电子公司的JEOL-2010型场发射高分辨透射电子显微镜(HR-TEM)进行分析. X射线光电子能谱(XPS)表征在Thermo ESCA LAB-250型光谱仪上测得, 真空度为 $1 \times 10^{-9} - 2 \times 10^{-10} \text{ torr}$, 用150 W单色Al K_α 射线($h\nu = 1486.6 \text{ eV}$)为激发源, 能量分析器固定透过能为20 eV, 结合能

通过表面积炭($C\ 1s = 284.8\text{ eV}$)进行电荷校正.

对于 H_2 还原- O_2 氧化循环测试,称取100 mg的样品于U形石英管中,在5% H_2/N_2 (45 mL/min)气氛下,以10 $^{\circ}C/min$ 的升温速率程序升温到600 $^{\circ}C$,采用TCD检测.在程序升温完成后,降温至100 $^{\circ}C$,切换气体至3% O_2/He ,吹扫10 min后升温到500 $^{\circ}C$,保持120 min.氧化结束后,降至室温,再将气体切换为 H_2/N_2 气氛,再次程序升温到600 $^{\circ}C$ 进行第二次循环测试.每次循环均包括 H_2 还原和 O_2 氧化两个过程.

CO 以及 CO_2 脉冲测试在Auto Chem II 2920 Micro-metrics化学吸附仪上进行,采用TCD检测器及质谱仪在线分析产物.

对于 CO 脉冲测试,称取50 mg样品置于U形管中.首先,样品在5% O_2/He (50 mL/min)气氛中400 $^{\circ}C$ 预处理30 min,然后 He 气吹扫,待基线走平后开始脉冲测试,测试条件为400 $^{\circ}C$,5% CO/He (30 mL/min)作为脉冲气.

对于 CO_2 脉冲测试,称取25 mg样品置于U形管中.样品首先还原预处理,还原条件为10% H_2/Ar (50 mL/min)混合气中,10 $^{\circ}C/min$ 程序升温到600 $^{\circ}C$ 保持30 min,之后 He 气吹扫30 min.降温到室温后,再次升温到50 $^{\circ}C$,以 He 气为载气,5% CO_2/He (30 mL/min)为脉冲气开始脉冲实验,每个脉冲相邻的间隔为2.5 min.

二氧化碳原位红外漫反射(CO_2 in-situ DRIFTS)在Thermo Nicolet Nexus 670型红外仪上进行,采用MCT检测器,高温样品池为 $ZnSe$ 窗口.样品先经过预处理再进行红外测试,预处理条件为:在500 $^{\circ}C$ 用10% H_2/N_2 (60 mL/min)气氛下还原30 min,之后降温到300 $^{\circ}C$ He 气预处理20 min.预处理结束后,降温到50 $^{\circ}C$, He (99.99%, 80 mL/min)吹扫下采集背景,之后通入5% CO_2/He (80 mL/min)气,同时开始采集数据.红外光谱的扫描范围为650–4000 cm^{-1} ,分辨率为4 cm^{-1} ,扫描次数为64次.DRIFTS的采样频率为每隔2 min采集一次.通 CO_2/He 气体20 min后,切换为 He 气吹扫,同时每隔2 min采集数据一次, He 吹扫时间为20 min.

3. 结果与讨论

3.1. XRD, BET和HR-TEM结果

图1为采用三种不同方法制备得到的 CeO_2 的XRD谱,所有样品都在600 $^{\circ}C$ 下焙烧3 h (1 $^{\circ}C/min$).从图中可见, CeO_2 样品均为立方萤石结构(JCPDS 34-0394), $Fm-3m$ 空间群.通过 N_2 吸附曲线测得样品 CeO_2 -GST, CeO_2 -nanorod和 CeO_2 -CA的比表面积分别为

79, 78和49 m^2/g .

图2为三种样品的TEM和HR-TEM照片.从图2(a)和(b)可见, CeO_2 -GST为纳米六面体颗粒,粒径在10–15 nm左右,高分辨透射电镜表明所暴露的晶面为稳定的(111)面.该形貌与文献报道的有所不同,因为在制备过程中水的引入会对形貌有很大影响,不同水的引入量会导致其形貌从球形变化为立方形,本实验中将铈源直接溶于乙二醇中未引入水,从而最终形成六面体形状^[23].图2(c)和(d)为 CeO_2 -nanorod的透射电镜和高分辨透射电镜图.从图中可以看到, CeO_2 -nanorod直径为20 nm左右,纳米棒的长度在100–300 nm不等.纳米棒主要沿着[110]轴生长,暴露出(100)面.对于柠檬酸法制备的 CeO_2 -CA样品,其没有规则形状,主要暴露出(111)面,粒径大小为5–20 nm.

3.2. XPS结果

采用XPS研究了焙烧前后 CeO_2 样品的表面性质(铈的价态以及表面氧空穴),结果见图3.通过分峰软件,对XPS谱图进行分峰拟合,并根据文献对拟合后的各个峰进行归属^[24–27]. $Ce\ 3d$ 的光电子能谱分为u和v两个系列的自旋-轨道多重谱.其中对应于 Ce^{4+} 的峰有6个,其中v (882.2–882.6 eV), v' (889.1–889.3 eV)和 v'' (898.2–898.5 eV)归属于v系列 $Ce\ 3d_{5/2}$ 的三个特征峰; u (900.6–901.0 eV), u' (907.5–907.7 eV)和 u'' (916.6–916.9 eV)对应于u系列 $Ce\ 3d_{3/2}$ 的三个特征峰. u' (903.5–904.2 eV)和 v' (885.1–885.8 eV)分别归属于 Ce^{3+} 的 $Ce\ 3d_{3/2}$ 和 $Ce\ 3d_{5/2}$ 的特征峰.其中 Ce^{3+} 含量见表1,其含量计算公式来自文献[24].

由图3(a)可以看出,对于 CeO_2 -GST样品,焙烧前其 Ce^{3+} 的含量为63%(表1),归属于 Ce^{3+} 的v'和u'出现强吸收,而归属于 Ce^{4+} 的u''峰强度很低.焙烧之后,样品表面仍有丰富的 Ce^{3+} ,含量为11.2%,且v'和u'的峰强度减弱,同时 Ce^{4+} 的特征峰u''出现(图3(b)).通过对比发现, CeO_2 -nanorod表面的v'和u'峰强度比其他两个样品弱很多,表面存在最少的 Ce^{3+} 含量.对拟合后的峰进行面积积分,计算出各个样品的 Ce^{3+} 含量(表1),其中 CeO_2 -nanorod表面 Ce^{3+} 含量最低,只有5%,柠檬酸法制备的 CeO_2 -CA样品表面的 Ce^{3+} 含量最高,为14.6%,这是由于柠檬酸在贫氧条件下分解出还原性气体,将 CeO_2 表面还原. CeO_2 -GST在焙烧之后,其表面 Ce^{3+} 含量仍能够保留为11.2%,是 CeO_2 -nanorod的两倍.从XPS结果可以证明,在乙二醇还原条件下制备得到的 CeO_2 -GST比传统的水热法制备的 CeO_2 样品具有更丰富的表面 Ce^{3+} ,从

而可以推断, CeO_2 -GST表面具有更丰富的氧空位^[28,29].

3.3. H_2 还原- O_2 氧化循环与CO-脉冲测试

为了测试所制备 CeO_2 样品可逆氧化还原的稳定性, 我们设计了 H_2 还原- O_2 氧化的循环实验. 样品储放氧速率通过CO-脉冲进行评价, 采用MS为检测器. 图4为三种样品的 H_2 还原- O_2 氧化循环图, 其耗氢量见表2. 由第一次 H_2 -TPR结果可见, CeO_2 -nanorod样品表现出最高的氢消耗量 $470 \mu\text{mol/g}$, 其次为 CeO_2 -GST ($380 \mu\text{mol/g}$), CeO_2 -CA最低, 为 $369 \mu\text{mol/g}$. 在后续的循环中, 三个样品的耗氢量均逐渐减小. 最终结果表明, CeO_2 -CA的稳定性最差, 在3次循环后, 其耗氢量降低到至 $118 \mu\text{mol/g}$; CeO_2 -nanorod与 CeO_2 -GST从第二次循环开始表现出相似的下降规律, 但是对循环测试后的 CeO_2 -nanorod样品进行TEM分析, 发现其棒状结构被破坏(图5(a)和(b)), 同时产生严重的烧结现象, 比表面积降低至 $6 \text{ m}^2/\text{g}$. 但是10次循环后的 CeO_2 -GST样品形貌没有发生太大变化(图5(c)和(d)). 因此 CeO_2 -GST样品在 H_2 还原- O_2 氧化的循环评价实验中表现出最优异的可逆氧化还原性能(图4a), 同时其结构在循环过程中也最稳定. 此外, 对于 CeO_2 -GST样品, 在第6次循环之后, 其耗氢量不再降低. CeO_2 表面丰富的氧空穴将有利于体相氧向表面的迁移, 从而使得耗氢量在循环过程中趋于稳定. 此外通过溶剂热法制备得到的 CeO_2 -GST能够提升材料结构的稳定性, 在10次循环后其结构仍能够保留.

图6为三个样品的CO-脉冲的MS谱图. 每个样品在16次脉冲内均达到饱和, 不再消耗CO. 从图6可以看出, 前10次脉冲3个样品的CO剩余量(峰面积)呈线性增加趋势, 在13次脉冲后CO均不再消耗. 对前10次脉冲的CO剩余量进行面积积分并对脉冲数做图, 其表现出很好的线性递增关系(图7(a), (b)和(c)). 在本试验中直线的斜率 k 应与样品的氧释放速率有关. 由于峰面积代表剩余的CO量, 因此样品对CO的消耗应该呈现相反的趋势, 即 k 越大, 样品的氧释放速率越慢. 三个样品的 k 值见表1, 其中 CeO_2 -nanorod的 k 值最小, 表明其氧释放速率最快, 而 CeO_2 -GST样品氧释放速率最慢.

根据第一性原理, 选择性暴露出(110)和(100)面有利于 CeO_2 表面形成氧空穴^[24–26]. 由HR-TEM结果可以发现, CeO_2 -nanorod选择性暴露出活性(100)晶面, 具有最快的氧迁移速率, 这一结论也与理论计算一致. CeO_2 -GST与 CeO_2 -CA均暴露出稳定的(111)面, 具有相对更慢的氧迁移速率. 进一步对后两种样品对比发现, 表面 Ce^{3+} 含量和氧迁移速率为 CeO_2 -GST < CeO_2 -CA,

CeO_2 表面具有更丰富的氧空穴, 同样能够提高其表面晶格氧的释放速率. Liu等^[15]通过研究表面富含氧空穴的纳米棒的CO催化活性也得出相同的结论. 因此可以推断, 通过控制合成条件制备富含表面氧空穴的 CeO_2 纳米材料将能够提高其氧的释放速率乃至催化活性.

3.4. CO_2 的捕获性能

对于 CO_2 的捕获一般采用有机胺溶液、薄膜吸附以及离子液体等^[30,31], 但其再生需要较高的能量, 而且生产升本高, 因而开发新的 CO_2 捕获材料具有十分重要的意义. CeO_2 是十分优良的路易斯碱, 从热力学上看, 将 CeO_2 用于 CO_2 的吸附是可行的^[30,32]. 此外, CeO_2 表面暴露出丰富的氧空穴时将有利于 CO_2 的吸附^[33]. 本文通过设计 CO_2 -脉冲实验来测试三种 CeO_2 材料吸附 CO_2 的性能, 同时采用原位DRIFTS来研究 CO_2 在 CeO_2 表面的吸附状态.

50°C 下 CO_2 的脉冲实验是通过TCD检测器来分析经过样品后剩余的 CO_2 含量的, 同时对尾气进行质谱分析, 确定实验过程中是否有CO产生. 质谱分析结果表明, 在 50°C 下没有CO特征信号出现, 只有很小的 CO_2 在28处的碎片峰. 图8为 CO_2 的MS信号. 可以发现在13个脉冲内所有样品对 CO_2 的吸附都达到饱和. 同时通过对 CO_2 信号的峰面积进行积分发现, CeO_2 -GST表现出最大的 CO_2 吸附量($149 \mu\text{mol/g}$), CeO_2 -nanorod和 CeO_2 -CA表现出相近的 CO_2 吸附活性, 分别为86和90 $\mu\text{mol/g}$.

通过 CO_2 原位DRIFTS对 CO_2 在 CeO_2 样品表面的吸附状态进行研究. 在DRIFTS实验前, 先对样品进行预处理, 预处理条件为在 500°C 通入10% H_2/N_2 混合气对样品进行预还原, 之后降温到 300°C 通入He吹扫30 min, 再降温到 50°C 并走基线以及采集背景. 之后通入5% CO_2/He 进行实验. 根据文献[34–39], 对所得谱图中的各个峰进行归属, 其结果汇总于表3中.

从图9(a)可以发现, 当 CO_2 进入样品池时, 在 $800\text{--}2000 \text{ cm}^{-1}$ 观察到6个强吸收峰, 分别位于856, 1021, 1217, 1289, 1397和 1584 cm^{-1} , 随着 CO_2 通入时间的延长, 各个峰的峰强度增加, 但没有新峰出现. 20 min后, 所有吸收峰强度都不再增加, 表明此时样品吸附饱和. CeO_2 -CA样品也表现出类似的吸附行为, 但是其峰强度要低于 CeO_2 -GST (图9(c)). CeO_2 -nanorod (图9(b))则表现出和前两个样品不同的红外吸收谱图, 首先在1214和 1392 cm^{-1} 处出现更强的吸收特征峰, 而且出现了一系列新的吸收特征峰, 分别位于1458, 1542和 1617 cm^{-1} . 对于 CeO_2 -GST和 CeO_2 -CA样品, 856, 1028, 1289和1584

cm^{-1} 处峰归属于双齿碳酸盐物种, 1217和 1397 cm^{-1} 归属于桥连碳酸盐物种. 对于 $\text{CeO}_2\text{-nanorod}$, 桥连碳酸盐物种的吸收峰分别红移至1214和 1392 cm^{-1} , 此外, 1612 cm^{-1} 处的吸收峰归属于重碳酸盐物种, 1458 cm^{-1} 处的吸收峰归属于单齿碳酸盐物种, 1542 cm^{-1} 处的吸收峰归属于甲酸盐物种^[35,36].

当再次通入He对样品表面吹扫10 min后, 样品的红外谱图出现明显的变化. 首先三个样品位于 1217 cm^{-1} 处归属于桥连碳酸盐的吸收峰明显减弱甚至消失, 这是由于桥连碳酸盐物种在 CeO_2 表面的吸附较弱, 很容易从表面脱附. 对于 $\text{CeO}_2\text{-nanorod}$ 样品, 位于 1584 cm^{-1} 的吸收峰消失, 同时在 1563 cm^{-1} 出现一个新的吸收峰. 有文献报道, 双齿碳酸盐在+3价Ce和+4价Ce表面的吸附峰存在差异, 其最强吸收峰 $\nu(\text{OCO})$ 在 Ce^{3+} 上为 1584 cm^{-1} , 而在 Ce^{4+} 上则会向低波数偏移至 1563 cm^{-1} ^[36], 因此可以推断出, $\text{CeO}_2\text{-nanorod}$ 表面 Ce^{3+} 被 CO_2 氧化生成 Ce^{4+} . 此外, $\text{CeO}_2\text{-nanorod}$ 样品归属于重碳酸盐、单齿碳酸盐和甲酸盐的特征峰在He吹扫下仍然保留. 同时通过对比桥连碳酸盐在三个样品上的吸附情况可以发现, 桥连碳酸盐物种在 $\text{CeO}_2\text{-nanorod}$ 表面的吸附最强, 其原因可能是高活性的(100)面更有利于桥连碳酸盐物种的稳定吸附. 对于 $\text{CeO}_2\text{-GST}$ 和 $\text{CeO}_2\text{-CA}$ 样品, 研究表明, CO_2 主要以双齿碳酸盐形式吸附, 没有观察到重碳酸盐物种.

通过对He吹扫后样品表面保留的吸附物种分析, $\text{CeO}_2\text{-nanorod}$ 由于暴露出活性的(100)面, 能够活化 CO_2

生成稳定的单齿碳酸盐、重碳酸盐和甲酸物种, 同时其表面的 Ce^{3+} 被 CO_2 氧化. 由于在该过程中没有发现CO的线式吸附峰, 同时结合在 CO_2 脉冲过程中同样没有跟踪到CO的特征峰, 可以认为 CO_2 主要以碳酸盐的形式在 $\text{CeO}_2\text{-nanorod}$ 表面被活化, 并不会直接生成CO. 同时红外光谱同样证明, CO_2 通过以不稳定的双齿碳酸盐物种吸附在 $\text{CeO}_2(111)$ 表面. 通过对比 $\text{CeO}_2\text{-GST}$ 和 $\text{CeO}_2\text{-CA}$ 的红外信号强度发现, $\text{CeO}_2\text{-GST}$ 具有更高的吸收强度, 这与其相对更高的 CO_2 吸附量对应, 归结为 $\text{CeO}_2\text{-GST}$ 具有相对更大的比表面积. CO_2 吸附过程中 Ce^{3+} 为活性位, 因此具有更高比表面积和丰富的表面 Ce^{3+} 的 $\text{CeO}_2\text{-GST}$ 更利于 CO_2 的捕获.

4. 结论

通过溶剂热法制备了 $\text{CeO}_2\text{-GST}$ 纳米材料, 其表面具有丰富的氧空穴, 且具有很好的可逆氧化还原性能. 这些丰富的氧空穴在高温条件下仍然能够得到保留, 从而促进了 CeO_2 的还原, 使得其在 $\text{H}_2\text{-TPR}$ 循环过程中表现出更好的循环稳定性. $\text{CeO}_2\text{-nanorod}$ 表现出相对较低的循环稳定性. CO_2 脉冲测试发现, $\text{CeO}_2\text{-GST}$ 表现出最好的 CO_2 吸附性能($149\text{ }\mu\text{mol/g}$). 此外, CO_2 在不同样品表面具有不同的吸附形式, 这与样品所暴露的晶面有一定关系. 双齿碳酸盐物种优先吸附在还原的(111)面; 而(100)面更利于桥式碳酸盐的吸附. 此外, 表面富含更多的氧空位和相对更大的比表面积更有利于 CO_2 的捕获.