Cu 掺杂铈基材料的乙醇完全氧化活性及热稳定性

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摘要: 考察了采用溶胶-凝胶法制备固溶体 $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ 和 $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ 样品的乙醇完全氧化(COE)性能. 采用 X 射线衍射(XRD)、BET 比表面积、拉曼(Raman)、氢气程序升温还原(H_2 -TPR)、光电子能谱(XPS)及电子顺磁共振(EPR)技术对样品结构进行了表征. 结果表明: 新鲜 $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ 样品的乙醇完全氧化活性优于 $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$; 样品经过老化处理后, 结果相反; Zr 的加入改善了样品的热稳定性. 此外, 还考察了乙醇完全氧化活性与活性物种之间的关系.

关键词: $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$; $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$; 乙醇完全氧化; 热稳定性

中图分类号: O643

Complete Oxidation of Ethanol and Thermal Stability of Ceria-Based Materials Modified by Doping Cu

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Abstract: The complete oxidation of ethanol (COE) was studied over $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ catalysts prepared by the sol-gel method. Samples were characterized by X-ray powder diffraction (XRD), Brunauer-Emmett-Teller (BET) adsorption, Raman spectroscopy, hydrogen temperature-programmed reduction (H_2 -TPR), X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance (EPR). Results show that for fresh samples, the activity of COE is found to be superior over $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ than over $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ whereas this is reversed for aged samples. The thermal stability improves after the introduction of Zr. Furthermore, the relationship between the active species and the activity for COE was investigated.

Key Words: $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$; $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$; Complete oxidation of ethanol; Thermal stability

Environmental problems associated with air pollution are now deteriorating our entire earth and represent some of the most formidable challenges facing global society in the future. Furthermore, limited energy sources warn of a potential lack of energy in the future. Environmental considerations and the energy crisis have led engineers and scientists to anticipate the need to

develop a clean, renewable and sustainable energy system. Presently, ethanol is considered as an alternative fuel extensively used in automobiles. The main reason for advocating ethanol is that it can be produced from nature products or waste materials compared with gasoline, which is only produced from non-renewable nature resources. The use of ethanol as fuel or fuel ad-

Received: December 30, 2009; Revised: March 5, 2010; Published on Web: May 13, 2010.

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The project was supported by the National High-Tech Research and Development Program of China (863) (2009AA064803).

国家高技术研究发展计划项目(863) (2009AA064803)资助

ditive can reduce the emission of conventional pollutants such as carbon monoxide, total hydrocarbon and NO_x , but may increase unburned ethanol and acetaldehyde emissions^[1-3]. These compounds are harmful to human health and considered as major contributors of environmental pollution. Hence, how to solve ethanol and acetaldehyde pollution problems has already become the major restriction of alternative fuels used widely.

Complete oxidation of ethanol (COE) catalysts has been studied for the control of the emissions from ethanol-fuelled vehicles by many researchers^[4-10]. Base metal oxides like CuO , MnO_x , CrO_x , and supported precious metal catalysts (Pt, Pd) have been used so far for COE. Precious metal catalysts are in general more active and tolerant to sulphur poisoning than base metal oxides. However, base metal oxide catalysts are much cheaper, allowing a higher loading. McCabe *et al.*^[4-5] found that a commercial hopcalite catalyst (CuO-MnO_2) exhibited comparable activity to $\text{Pt/Al}_2\text{O}_3$ for ethanol oxidation. Wahlberg *et al.*^[6] found that catalysts containing Cu and Cu-Mn were more selective for COE than precious metal. Larsson *et al.*^[9] found that the interaction between cerium and copper resulted in improved reducibility of the active copper species, which is considered to be determinant for the activity of COE.

Copper oxides and supported copper materials have been studied in many fields, such as the combustion of CO and CH_4 ^[11-13], the water-gas shift reaction^[14-15], and the wet oxidation of phenol^[16]. According to Kato *et al.*^[17], Cu-containing catalyst involves a large volume change during oxidation/reduction process that leads to fragmentation of the catalyst. Noronha *et al.*^[18] have observed that precious metal particles were covered by base metal oxide for Pd-based catalyst for oxidation of ethanol. Therefore, it is necessary that the base metal ions are fixed and retain immobile, especially after thermal treatment, which may reduce the negative effect on precious metal catalysts for oxidation of ethanol. Further, it has been reported that doping with Zr(IV) can control the structure or the sites of ceria crystallite, which causes the improvement in the oxygen storage capacity, thermal stability, and redox property^[19]. To the best of our knowledge, few literatures have been reported on the comparative study of Cu-Ce-O and Cu-Ce-Zr-O catalysts for the COE, especially after high-temperature treatment. The present work investigates Cu-Ce-O and Cu-Ce-Zr-O samples in the form of solid solution for the COE. The microstructure and the thermal stability were characterized by XRD, Raman, TPR, XPS, and EPR. And the relationship between structure properties and the activity of COE was proposed.

1 Experimental

1.1 Sample preparation

Cu-doped ceria-based mixed oxides ($\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$) were synthesized by sol-gel method using citric acid as chelating agent. The corresponding Ce(III) (Zibo Rongruida), Zr(IV) (Zibo Rongruida), and Cu(II) (Tianjin Kewei) nitrates were of high purity over 99.9%. The citric acid was used

as complex agent, and glycol was used as additive. After continuous stirring for 2 h, the mixed solution was treated at the temperature of 353 K overnight to form the sponge yellow gel. Then, the gel was dried at 373 K for 3 h and milled before calcinations. The dried gel was calcined at 573 K for 30 min and then at 773 K for 5 h. In this way, the fresh sample was obtained. The samples were further calcined at 973 and 1073 K in air for 3 h and referred to as $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (973 K), $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (1073 K), $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (973 K), $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (1073 K).

1.2 Characterization

The X-ray powder diffraction (XRD) patterns were acquired with an X'Pert Pro diffractometer (Netherlands) operating at 40 kV and 40 mA with ferrum-filtered $\text{Co } K_\alpha$ radiation and ranging from 20° to 90° with a step size of 0.030° .

The specific surface area of the sample was measured by the BET method using N_2 adsorption/desorption (Quantachrome NOVA2000, America) at 77 K.

The Raman spectra of the powder samples were recorded with a Bruker FS100 FT-Raman spectrometer (Germany) and a liquid- N_2 -cooled super InGaAs detector. The spectra were excited with a diode pumped YAG laser (1064 nm) with a power of 100 mW.

H_2 -TPR experiments were performed using a Micromeritics AutoChem 2910 (America). The catalyst was first purged under N_2 ($30 \text{ mL} \cdot \text{min}^{-1}$) at 473 K for 1 h and then cooled to room temperature. The sample was then exposed to a flow of 5% H_2/Ar ($30 \text{ mL} \cdot \text{min}^{-1}$) while the temperature was ramped from room temperature to 1173 K at a rate of $10 \text{ K} \cdot \text{min}^{-1}$.

X-ray photoelectron spectroscopy (XPS) analyses were conducted with PHI-1600ESCA spectrometer (America) with a non-monochromatic $\text{Mg } K_\alpha$ ($h\nu = 1253.6 \text{ eV}$) radiation source operated at 15 kV and 400 W. The background pressure in the XPS chamber was kept below $0.67 \times 10^{-6} \text{ Pa}$. The binding energy (E_B) was calibrated based on the line position of C 1s (284.6 eV).

Electron paramagnetic resonance (EPR) spectra at the X band frequency ($\approx 9.7 \text{ GHz}$) were recorded at room temperature with a Bruker A320 spectrometer (Germany) calibrated with 2,2-diphenyl-1-picrylhydrazyl ($g = 2.0036$). Portions of same mass of samples were placed inside the quartz probe cell. The EPR parameter values have been precisely determined from the calculated spectra. g factor was determined by the equation, $h\nu = g\beta H$, where h is Planck constant, H is the applied magnetic field, β is Bohr magneton.

1.3 Activity test

The catalysts were tested in a fixed bed reactor made of a quartz tube. A catalyst sample was packed and sandwiched between two quartz wool plug. The feed was a mixture of air and ethanol (1.5%) with a space velocity of 30000 h^{-1} . The concentration of CO_2 was measured as a function of temperature on line by IR (America). The temperature at 50% yield CO_2 is used as a measure of ethanol oxidation activity and is denoted as T_{50} .

2 Results and discussion

2.1 XRD analysis

Fig.1 XRD patterns for different samples

Fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ samples were calcined at 973 and 1073 K in air for 3 h and referred to as $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (973 K), $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (1073 K), $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (973 K), and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (1073 K).

Powder X-ray diffraction patterns of different samples are shown in Fig.1. For fresh Cu-doped samples (Fig.1a), a single fluorite-type phase ($Fm\bar{3}m$ space group) was found, there are no characteristic reflections of CuO phase found. We have previously reported^[20] that it may be due to the high dispersion of the CuO nanoparticles with too small particle sizes on the surface of the support to be identified by the conventional X-ray diffraction method, or the localization of Cu^{2+} ions in the solid solution^[21]. After aging treatment, the XRD patterns for all samples show narrower diffraction line with respect to their respective counterpart, which indicated the increased crystallite size. It should be noted that a visible CuO phase at about $2\theta = 41.6^\circ$ and 45.4° can be identified in the XRD patterns of $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (973 K), $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (1073 K), $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (1073 K) samples, while $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (973 K) sample remains a single fluorite lattice structure. It indicated that the introduction of Zr improve the thermal stability of sample and restrain the deactivation after aging treatment.

The lattice parameters calculated by Bragg's equation are listed in Table 1. For the $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ samples, the introduction of Cu causes the shrink of the lattice due to its relatively smaller ion radius (0.072 nm) with respect to Ce^{4+} (0.103 nm). It is worth noting that the $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (0.5324 nm) sample shows much smaller lattice parameter than that of $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (0.5399 nm), indicating the synergistic effect of Zr(IV) and Cu(II) shrink the

lattice for their smaller ion radii. After aging treatment, obvious expansion of the lattice was observed compared with the fresh ones, indicating a segregation of Cu^{2+} to form other compounds.

The averaged crystallite sizes determined by Scherrer equation are listed in Table 1. As listed in Table 1, the average crystallite sizes of the fresh samples are 9.3 and 6.3 nm for $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$, respectively. After high temperature calcinations, the aggregation of crystals took place, and then the average crystallite size increased to 61.0 and 18.8 nm, respectively. Interestingly, the increasing amplitude of the average crystallite size for $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ is much smaller than that of $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ catalyst after aging treatment. So, it was considered that the introduction of zirconia is more effective for improving the thermal stability.

Evolution of specific surface areas of Cu doping samples is presented in Table 1. It can be found that a significant loss of surface area is observed after high-temperature treatment. It is worth noting that the catalytic activity of ceria-based material does not depend directly on its surface area. According to Monte *et al.*^[22], the participation of bulk oxygen to reduction processes in ceria-based materials makes surface effects less important.

2.2 Raman spectral analysis

In contrast to the XRD results, which yield information related mainly to the cation sublattice, Raman spectra of these fluorite-type oxide structures are dominated by oxygen lattice vibra-

Table 1 BET special surface area, lattice parameters^a and crystal sizes^b of different samples

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$		Lattice parameter (nm)		Crystallite size (nm)	
	fresh	aged at 1073 K	fresh	aged at 1073 K	fresh	aged at 1073 K
$\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$	25	4	0.5399	0.5400	9.3	61.0
$\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$	41	2	0.5324	0.5328	6.3	18.8

^aThe lattice parameters were calculated based on Bragg's law; ^bCrystal size was determined by the Scherrer equation calculated based on the (111) plane.

Fig.2 Raman spectra observed at rom temperature on fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (a), $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (1073 K) (b), fresh $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (c), and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (1073 K) (d)

tions, which are sensitive to the crystalline symmetry, being thus a potential tool to obtain additional structure information. The Raman profiles of all samples are shown in Fig.2. As reported in previous study^[20], for pure CeO_2 , there is a peak at 464.2 cm^{-1} ascribed to the F_{2g} mode of fluorite (Fig.2(a)). And for fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ sample, the dominant peak shifts to lower frequency accompanying with reduced intensity (Fig.2(c)). Two reasons contribute to the frequency shifts^[23]. The first is increased oxygen vacancies; the second is dilation or contraction of the lattice. The lattice variation indicates that some defects are generated. The presence of lattice defects induced the mobility of oxygen, which are favorable for the redox activity. Compared with fresh sample, the F_{2g} band of aged sample shifted to higher frequency can be observed due to the expansion of the lattice, indicating the breaking of symmetry of the M—O bond^[24].

For the $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_x$ sample, in addition to the dominant band at 473.8 cm^{-1} , ascribed to the F_{2g} mode of fluorite, two minor peaks centered at around 298.3 and 620.4 cm^{-1} appeared, as shown in previously study^[20]. We have reported that the appearance of weak bands around 298.3 and 620.4 cm^{-1} , which is attributed to the tetragonal displacement of the oxygen atoms from the ideal fluorite lattice positions, indicates the formation of phase t' or t'' ^[20,25]. This was considered as a potential active structure for the ceria-zirconia solid solution. After doping Cu, the dominant peak shifts to 476.1 cm^{-1} , and the other peaks are located at 304 and 638 cm^{-1} , respectively. It is obviously that the Raman spectrum of $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ is very similar to that of $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$, which indicates that the doping of Cu gives little influence on the structure of $\text{Ce}_{0.67}\text{Zr}_{0.33}\text{O}_2$ ^[20]. Namely, Cu species were incorporated into the CeO_2 lattice forming solid solutions, or the Cu species were highly dispersed on the surface of ceria-zirconia in agree with results of XRD. After aging treatment, the F_{2g} band slightly shifted to lower frequency due to cell expansion, which is in line with the increased cell parameter.

2.3 Activity of COE

Result of activity tests, the temperature at 50% yield CO_2 (T_{50}), are shown in Fig.3. For fresh samples, T_{50} is lower over $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ than that over $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$. According to Wang *et*

Fig.3 T_{50} for COE with ethanol (1.5%)+air (98.5%), a space velocity of 30000 h^{-1} over fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (a), $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (1073 K) (b), fresh $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (c), and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (1073 K) (d)

al.^[26], the dispersed CuO was responsible for the higher catalytic activity of the COE. Compared with $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ sample, the fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ sample is characterized with a higher CuO dispersion degree and a lower reduction temperature confirmed by the TPR and EPR analysis. So the fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ sample shows superior activity for COE. After aging treatment, the activity of COE was badly decreased. Based on Stobbe^[27] and María^[28] *et al.*, the oxides with high degree of crystallinity had a pronounced decrease in the catalytic activity. For aged samples, T_{50} of COE over $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ is lower than that over $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$. The T_{50} over aged $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ is increased by 117 K, whereas the corresponding value is 76 K for $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$. It indicated that $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ is less stable and is easily deactivated against thermal treatment. The addition of Zr improved the thermal stability, which can prevent mixed oxides from reaching a crystalline structure. So the aged $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ sample retained more activity for the ethanol complete oxidation.

2.4 H₂-TPR analysis

TPR profiles of all samples are presented in Fig.4. As reported in previous study^[20], the CuO has one reduction peak at 591 K. And for CeO_2 , two reduction peaks located at 784 and 1074 K attributed to the release of surface oxygen and bulk oxygen, respectively. While for fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ sample, two new strong

Fig.4 H_2 -TPR profiles of fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (a), $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (1073 K) (b), fresh $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (c), and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (1073 K) (d)

Fig.5 XPS patterns of Cu 2p and O 1s for fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (a), $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (1073 K) (b), fresh $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (c), and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (1073 K) (d)

reduction peaks (α and β) at about 434 and 458 K are appeared, which can be ascribed to the reduction of the finely dispersed CuO and the Cu^{2+} in the $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ solid solution. In addition, two reduction peaks around 718 and 1052 K ascribed to the release of bulk and surface oxygen (γ) and lattice oxygen (δ) are still evident, and shift to lower temperature compared with CeO_2 . It can be considered that the introduction of Cu improve the low-temperature activity of CeO_2 . After aging treatment, the intensity of low-temperature peaks (α and β) is weakened, meanwhile new reduction peaks attributed to the reduction of bulk CuO is occurred^[29].

For $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ samples, the low-temperature peaks (α and β) shift to lower temperature in comparison with its counterpart due to the synergistic effects between CuO and the ceria-zirconia^[20]. According to literature^[9], the reduction of the finely dispersed CuO (α) is maybe as the active sites for COE. Compared with $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$, the addition of Zr leads to the decrease of the “ α ” peak intensity. The amount of H_2 uptake at the “ α ” peaks is calculated to be $548 \mu\text{mol} \cdot \text{g}^{-1}$ catalyst for $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$, while $264 \mu\text{mol} \cdot \text{g}^{-1}$ catalyst for $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$, which suggested that the quantity of CuO species dispersed on the surface of $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ is much more than that on $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ sample. This may explain the higher activity of complete oxidation ethanol for fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ than that for fresh $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$. For the aged samples, the $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ sample shows superior thermal stability to $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ confirmed by XRD analysis, which is believed to be essential for the better activity of COE.

2.5 XPS analysis

In order to obtain more information on the state of copper species, XPS spectra were recorded for all samples as shown in Fig.5. According to literature^[13,30], the presence of the shake-up peak and a higher Cu $2p_{3/2}$ binding energy (933.0–933.8 eV) are two major XPS characteristics of CuO, while a lower Cu $2p_{3/2}$ binding energy (932.2–933.1 eV) and the absence of the shake-up peak are characteristics of reduced copper species. As shown in Fig.5, the fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ sample contained a shake-up peak of weak intensity at 939–944 eV and the Cu $2p_{3/2}$ peak was centered at about 932.7 eV. The value is lower than the Cu 2p binding energy of CuO (933.6 eV). The lower Cu $2p_{3/2}$ binding ener-

gies (932.7 eV) and the low intensity of the shake-up satellite structure suggest that the presence of active copper species in the $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ sample, which may be Cu^+ or Cu^{2+} species^[20]. According to Avgouropoulos *et al.*^[13], both Cu^{2+} and Cu^+ species present in CuO- CeO_2 catalysts prepared with various methods confirmed by Cu L₃VV Auger kinetic energy. It may be suggested that the reduced copper species such as Cu^+ exit on the surface of the catalyst besides Cu^{2+} species. The formation of Cu^+ species can be derived from the strong interaction of the copper clusters with ceria. It is worth noting that the Cu 2p XPS spectra for aged $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ samples contained a shake-up peak of weak intensity at 939–944 eV and the Cu $2p_{3/2}$ peak was centered at about 933.0 eV. It suggested that the presence of some bulk CuO on the surface of catalysts, is in agreement with the XRD results.

As shown in Fig.5, it can be observed O 1s spectra display two main features, the major contribution at $E_B \approx 529.3$ eV corresponds to lattice oxygen species in fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ samples, the broad peak with $E_B \approx 531.5$ eV can be attributed to adsorbed oxygen. By fitting the O 1s peak with two set of oxygen species, we have previously found that the fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ sample has almost the same amount of adsorbed oxygen species (21.1%) with respect to the fresh $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (21.6%)^[20]. Therefore, the effect of oxygen species over different samples on activity for COE is similar between the fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$. After aging treatment, the amount of adsorbed oxygen species for the aged $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ are 24.8% and 34.0%, respectively. So the adsorbed oxygen species over aged $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ sample for the COE is more contributive than that of the aged $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ sample.

2.6 EPR analysis

EPR spectra of $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ samples are shown in Fig.6. Each spectrum is composed of three signals which can be attributed to monomers, dimers, and clusters of Cu^{2+} . Based on the literature^[20,31–33], the A_1 signals was attributed to isolated Cu^{2+} ions located in octahedral sites in ceria with a tetragonal distortion and surrounded by more than six ligands. The A_2 signal was attributed to Cu^{2+} in form of clusters. And the sig-

Fig.6 EPR spectra observed at room temperature on fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (a), $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ (1073 K) (b), fresh $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (c), and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ (1073 K) (d)

nal K in the spectra corresponds to $\text{Cu}^{2+}\text{-Cu}^{2+}$ ion pairs arising from the coupling between unpaired electrons of two Cu^{2+} ions. After aging treatment, some changes have taken in the characteristics of the EPR spectrum of the catalysts. Formation of CuO crystallites on the catalyst surface can decrease the effective intensity of the isolated Cu^{2+} signal^[26]. As shown in Fig.6, there is no significant difference in the intensity of the Cu^{2+} signal for fresh and aged $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ samples. However the difference for fresh and aged $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ samples is visible. It indicated the better thermal stability for $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ sample, in agreement with the XRD analysis. Furthermore the abatement of K signal in low magnetic field indicates the decrease of Cu^{2+} ion pairs in the lattice of CeO_2 , which reveals that Cu^{2+} ion pairs possess higher reducibility.

3 Conclusions

In summary, $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ and $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ were synthesized by sol-gel method, investigated for the structure characteristics, thermal stability, and the activity for COE. Fresh $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ sample enriched with well-dispersed CuO species, shows higher performance for COE than $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$, the role of well-dispersed CuO on the catalysis activity may be important. The aged $\text{Cu}_{0.1}\text{Ce}_{0.6}\text{Zr}_{0.3}\text{O}_x$ sample is more active for the ethanol oxidation than that for the aged $\text{Cu}_{0.1}\text{Ce}_{0.9}\text{O}_x$ because the addition of Zr improved the thermal stability, sintering may be the major factor that leads to the activity variation for aged sample.

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