Influence of Ce/Zr Ratio on the Synergistic Effect over $\text{CuCe}_{1-x}\text{Zr}_x\text{O}_y$ /ZSM-5 Catalysts for the Self-Sustained Combustion of Carbon Monoxide

Ruozhu Zhao, Qinglan Hao, Feng Bin, Running Kang & Baojuan Dou

To cite this article: Ruozhu Zhao, Qinglan Hao, Feng Bin, Running Kang & Baojuan Dou (2017) Influence of Ce/Zr Ratio on the Synergistic Effect over $\text{CuCe}_{1-x}\text{Zr}_x\text{O}_y$ /ZSM-5 Catalysts for the Self-Sustained Combustion of Carbon Monoxide, Combustion Science and Technology, 189:8, 1394-1415, DOI: [10.1080/00102202.2017.1297807](https://doi.org/10.1080/00102202.2017.1297807)

To link to this article: <http://dx.doi.org/10.1080/00102202.2017.1297807>

Accepted author version posted online: 03 Mar 2017.
Published online: 03 Mar 2017.

Submit your article to this journal [↗](#)

Article views: 36

View related articles [↗](#)

View Crossmark data [↗](#)

Influence of Ce/Zr Ratio on the Synergistic Effect over $\text{CuCe}_{1-x}\text{Zr}_x\text{O}_y/\text{ZSM-5}$ Catalysts for the Self-Sustained Combustion of Carbon Monoxide

Ruozhu Zhao^{a,b}, Qinglan Hao^a, Feng Bin^{b,c}, Running Kang^{b,c}, and Baojuan Dou^d

^aCollege of Chemical Engineering & Materials Science, Tianjin University of Science & Technology, Tianjin, PR China; ^bState Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Science, Beijing, PR China; ^cCollege of Metallurgy and Energy, North China University of Science and Technology, Tangshan, PR China; ^dCollege of Marine & Environmental Sciences, Tianjin University of Science & Technology, Tianjin, China

ABSTRACT

The self-sustained combustion of CO was studied over a series of $\text{CuCe}_{1-x}\text{Zr}_x\text{O}_y/\text{ZSM-5}$ catalysts with different Ce/Zr molar ratios to evaluate the correlation of their structural characteristics with catalytic performance. The obtained results demonstrated that the activity of the cerium-containing catalysts was much higher than that of the CuZr_1/Z , with the activity of CO combustion following the order: $\text{CuZr}_1/\text{Z} < \text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z} < \text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z} < \text{CuCe}_1/\text{Z} < \text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$. After cerium addition, the cerium-zirconium mixed oxides formed promoted the copper species well dispersed on the catalyst surface. The high activities of cerium-containing catalysts were closely related to the synergetic effects among the copper, cerium, and zirconium species, as the surface copper species provided sites for CO adsorption and the cerium-zirconium mixed oxides promote the activation of oxygen. The activities were probably also attributed to some copper species present as substitutional defects in the ceria lattice, which were more reducible than the copper clusters, microcrystals, and bulk CuO particles. The $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ possessed excellent redox capacity, adsorption/activation properties for O and CO species, and therefore induced a self-sustained combustion of CO at the lowest temperature than that of other $\text{CuCe}_{1-x}\text{Zr}_x\text{O}_y/\text{ZSM-5}$ catalysts.

ARTICLE HISTORY

Received 30 November 2016

Revised 16 February 2017

Accepted 17 February 2017

KEYWORDS

Carbon monoxide; Ce/Zr ratio; $\text{CuCe}_{1-x}\text{Zr}_x\text{O}_y/\text{ZSM-5}$ catalysts; Self-sustained combustion

Introduction

Basic oxygen furnace (BOF) steelmaking is one of the key processes in the steel industry accounting for over 60% of the total steel production in the world (Shao et al., 2014). The principle of the BOF is to blow pure oxygen into liquid iron to decrease carbon contents and other impurities. The off-gas produced contains a considerable amount of CO, which is generally collected as a fuel to reheat steel in the rolling mills (Landi et al., 2013). Because a high concentration of oxygen in combination with CO is liable to cause explosions, the off-gas generated at steelmaking intermissions is not directly recovered

CONTACT Feng Bin binfeng@imech.ac.cn State Key Laboratory of High-Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Science, Beijing 100190, China; Baojuan Dou bjdou@tust.edu.cn College of Marine & Environmental Sciences, Tianjin University of Science & Technology, Tianjin 300457, China.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gcst.

as a fuel, but is often discharged into the atmosphere (Li et al., 2011b). To conserve the energy that could have been discharged, catalytic post-combustion, in fact, promotes the full and efficient oxidation of CO at temperatures far lower than those established in typical flames, and thereby is considered to be an effective strategy to produce heat suitable for electric power generation (Lundgren et al., 2013).

Self-sustained catalytic combustion has previously received significant attention in different regimes. The fuel/oxygen mixture is first catalyzed to generate local hot spots on the catalyst surface. Due to the rate of heat generation far exceeding the rate of heat loss to the surroundings, such exothermic chemical reactions of fuel oxidation and resultant temperature rise leading to catalytic ignition (Bin et al., 2015). Veser et al. (1999) investigated the ignition behavior of simple alkanes with air on Pt, Pd, Rh, and Ir foil catalysts, with results indicating that the ignition temperatures are associated well with the C–H bond energy of alkanes and the metal–oxygen bond energy of noble metals. Based on Pt/Al₂O₃, Pt/TiO₂, and Pt/SiO₂ catalysts, Alayon et al. (2009) believed that the catalyst at low activity is metallic covered with CO, which hampers oxygen from reacting. But the results also showed that the depletion of CO at high activity enables oxygen to interact with the surface, and enhances the catalytic activity by changing the rate-limiting step until realizing the self-sustained combustion. Mhadeshwar and Vlachos (2005) have studied the CO ignition using Rh catalysts, with test results indicating that the ignition temperature of CO/O₂ mixtures increases from 147°C to 157°C when the inlet CO composition varies from 4% to 9%. According to Aghalayam et al. (2000), the ignition temperature (135–152°C), obtained at a fixed CO/O₂ ratio of 1.0 for various N₂ dilution levels, is relatively unaffected by dilution. Although noble metals are often employed, the high cost and low thermal stability limit its application as usual (Kolobova et al., 2017).

Much attention has been paid to copper-based ceria-zirconia solid solutions (Liu et al., 2010). On one hand, the CO tends to be adsorbed on surficial Cu sites of catalysts because the d orbitals of copper ions are completely or nearly full, and thus can form strong bonds with CO. On the other hand, the Ce_xZr_{1-x}O₂ solid solution conduces to shape structural defects due to substitution of Ce⁴⁺ by Zr⁴⁺, thus further enhances the oxygen mobility through the lattice, redox property, and sintering-resistant of CeO₂ (Laguna et al., 2015). The performance of these catalysts is found to be strongly dependent not only on the molar ratio among reagents but also on the morphological and structural characteristics of the materials that can influence both the interaction between the oxides and the dispersion of the active phases (Moretti et al., 2011, 2015).

Herein, our contribution of this study to the knowledge of CuCe_xZr_{1-x}O_y/ZSM-5 catalysts is to show the effect of the Ce/Zr ratio on the physico-chemical properties of catalysts and its influence on the improved catalytic response toward low-temperature activity of CO oxidation, in order to cope with a low exhaust temperature of BOF. Here, the ZSM-5 zeolite is employed as the support due to its excellent thermal stability and good dispersion to active species. The structural and textural properties, redox behavior, CO/O adsorption, and metal support interaction were determined by the combination of several characterization techniques: X-ray powder diffraction (XRD), ultraviolet–visible diffuse reflectance spectra (UV–vis DR), X-ray photoelectron spectroscopy (XPS), H₂ temperature-programmed reduction (H₂-TPR), temperature-programmed desorption of CO/O₂ (CO/O₂-TPD), and in-situ diffuse reflectance Fourier infrared transform (in-situ DRIFT). The catalytic performance for the self-sustained combustion of CO was tested via

a temperature-programmed oxidation process. The possible mechanism for the catalytic oxidation reaction was proposed from experimental data.

Experimental

Catalyst preparation

The series of $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts ($x = 0, 0.25, 0.5, 0.75$, and 1 , denoted as $\text{CuCe}_x\text{Zr}_{1-x}/\text{Z}$) were prepared by a wet impregnation method. A desired amount of copper acetate, zirconyl nitrate, and cerium nitrate were added to deionized water and mixed with H/ZSM-5 powder (Si/Al atomic ratio = 25) at room temperature. The resulting solution was stirred at 80°C for 24 h. After being dried by evaporation, the samples were calcined at 600°C for 4 h. The Cu content of the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts was fixed at 2.0 wt%, and the molar ratio of $\text{Cu}/(\text{Ce}+\text{Zr})$ was 1:1.

Characterization

The crystalline phase was determined by powder XRD using a Rigaku D/MAC/max 2500 v/pc instrument with Cu K α radiation (40 kV, 200 mA, $\lambda = 1.5418 \text{ \AA}$). Diffractometer data were acquired with a step size of 0.02° for 2θ values from 5° to 70° . UV-vis DR spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. The measurements have been performed in the range of 200–1000 nm with a resolution of 2 nm for the samples diluted in KBr. XPS was obtained with a Kratos Axis Ultra DLD spectrometer using an Mg K α radiation. The binding energies were referenced to the C 1s line at 284.6 eV from adventitious carbon.

Redox properties were studied by H_2 -TPR using a TPD/R/O instrument (Micromeritics 2920 II). The treatment of the solid (200 mg) was carried out in a 20 vol% O_2 gas flow at 600°C for 1 h. The thermo-reduction process was performed by passing a 5 vol% H_2/He gas mixture (50 mL/min) through the sample while heating from 50°C to 600°C (ramping rate $10^\circ\text{C}/\text{min}$). TPD of CO or O_2 was also carried out on the Micromeritics 2920 II analyzer. About 200 mg of sample were used. After O_2 or CO (30 mL/min) saturation in 1 h, the gas was switched to Ar for 0.5 h. Subsequently, TPD was performed by ramping the temperature at $10^\circ\text{C}/\text{min}$ to 900°C in He (30 mL/min).

In-situ DRIFT measurements were obtained on the Bruker Tensor 27 spectrometer. Before recording spectra, the sample disk placed in the DRIFT cell was pretreated in a flow of Ar at 400°C and subsequently cooled to 150°C for taking a reference spectrum. The reaction gas mixture (10 vol% CO, 15 vol% O_2 , N_2 balance) was fed to the sample at a total flow rate of 30 mL/min. For each temperature step, the DRIFT spectra of reaction were sequentially recorded (64-scan accumulation and 4 cm^{-1} resolution).

Catalytic activity test

Catalytic experiments were performed in a conventional fixed bed reactor under atmospheric pressure. The catalysts (20–40 meshes) were placed into a quartz reactor of 4 mm i.d. The thermocouple was located between the reactor wall and the oven wall, and was used to control the oven temperature. During each temperature-programmed oxidation

(TPO) run, the heating/cooling rate was fixed at 5°C/min. The oven temperature programmed oxidation has been employed in our work in order to investigate the activity of catalysts, such as ignition temperature, reaction rate, etc. In real flow reactors, the catalyst is heated by the gas flow rather than the oven. When the catalyst bed is heated by gas flow to reach the gas ignition temperature, the self-sustained combustion of CO can be started. To evaluate the activity of the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts, the weight of the catalyst was 240 mg, and the total flow rate of the reaction mixture was 500 ml/min. The feed gas contained 10 vol% CO + 20 vol% O_2 and N_2 as balance. The effect of CO, O_2 , and CO_2 on the reaction was examined with addition of 1 vol%, 3 vol% or 5 vol%, 7 vol%, 10 vol% CO; 3 vol%, 4 vol%, 5 vol%, 10 vol%, 15 vol% O_2 ; 0 vol%, 30 vol%, 40 vol%, and 75 vol% CO_2 , respectively. In order to determine the effect of catalyst weight and flow rate, 120 mg, 240 mg, 480 mg catalysts; 0.25 l/min, 0.5 l/min, 0.75 l/min, and 1.0 l/min flow rates were carried out, respectively. The effluent CO, O_2 , and CO_2 detected by an online gas analyzer (QGS-08, Maihak).

Results and discussion

Chemical nature of copper, cerium, and zirconium species

The XRD powder patterns of the parent ZSM-5 sample and samples doped with copper, cerium, and zirconium are shown in Figure 1. The ZSM-5 shows the typical diffraction peaks at $2\theta = 7.9^\circ$, 8.8° , 23.1° , and 23.8° (PDF 44-0003), representing (011), (200), (051), and (303) planes of crystal structures, respectively. This is unchanged after the metal introduction, indicating that the original zeolite structure remains intact. However, the intensity of the ZSM-5 principal diffraction peaks decreases remarkably after the copper, cerium, and zirconium are loaded, due to the higher absorption coefficient of metal compounds for the X-ray radiation and the lower zeolite content in the samples by the metal addition. In the case of the CuZr_1/Z , $\text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z}$, $\text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z}$, and $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ samples, no diffraction peaks attributed to metal oxides are observed, which suggests that the copper, cerium, and zirconium species are homogeneously dispersed on the ZSM-5 support at $x \leq 0.75$. The presence of cubic CeO_2 ($2\theta = 28.2^\circ$, PDF = 34-0394) on the CuCe_1/Z sample is assessed, with a mean diameter of 5 nm estimated according to the Scherrer equation.

The information on the surface electronic states can be obtained from UV-vis diffuse reflectance measurements. Figure 2 displays three absorption bands at 214, 270, and 358 nm for the CuZr_1/Z , as well as a broad and weak band at 550–1000 nm. The absorption band at 214 nm and 270 nm can be assigned to oxygen-to-metal charge-transfer related to the Cu^+ or Cu^{2+} ions doped and stabilized in the framework of zeolite (Zhou et al., 2013). The band at 270 nm appears asymmetric, and the shoulder centered at 358 nm corresponds to the transitions of Cu^{2+} in tetragonal oxygen configuration (Liang et al., 2012), which can be related to copper clusters dispersed on the ZSM-5 surface. Eight coordinated tetravalent zirconium species are also responsible for the absorption in the range of 200–220 nm (Postole et al., 2010). The band at 550–1000 nm corresponds to the CuO phase, due to the Cu^{2+} transition in octahedral oxygen configuration (Praliaud et al., 1998). After the cerium addition, the band at 270 nm is overlapped by the characteristic absorption of CeO_2 at 285 nm, assigned to $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$ charge transfer transitions (Sinha

Figure 1. XRD patterns of $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{Z}$ catalysts with different loading ratios: (a) CuZr_1/Z , (b) $\text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z}$, (c) $\text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z}$, (d) $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$, and (e) CuCe_1/Z .

and Suzuki, 2005), and this absorption strengthens with cerium content. Because of the electron interaction between copper and cerium ions, however, UV-vis cannot distinguish between each of them. The position of adsorption is 358 nm, 389 nm, 450 nm, 451 nm, and 472 nm for CuZr_1/Z , $\text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z}$, $\text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z}$, $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$, and CuCe_1/Z in sequence. The position and intensity of those adsorptions keep direct linear relationship with the composition, as the enhanced concentration of the oxygen vacancies in composite oxides system forms a defect band that further changes the energy of the conduction band (Lukac et al., 2007). Furthermore, the visible light absorption (600–800 nm) corresponding to the CuO phase shifts toward low wavelength direction with the cerium content increasing, indicating the enhancement of copper oxide dispersion after zirconium introduction.

XPS analysis

XPS is performed in order to further illuminate the surface composition and the chemical state of the elements existing in the catalysts. As shown in Figure 3A, the Cu 2p spectrum of the CuZr_1/Z catalyst shows two main peaks that are attributed to Cu 2p_{3/2} and Cu 2p_{1/2} at about 933.8 eV and 954.3 eV, respectively. Due to considerable asymmetry of the Cu

Figure 2. UV-vis DR spectra of the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts with different loading ratios: (a) CuZr_1/Z , (b) $\text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z}$, (c) $\text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z}$, (d) $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$, and (e) CuCe_1/Z .

$2p_{3/2}$ peak, peak deconvolution and fitting to experimental data indicate that the Cu $2p_{3/2}$ peak could be fitted well by two peaks corresponding to the chemical states of Cu^{2+} at 934.6 eV with a shake-up peak located at 938–946 eV and Cu^+ at 933.1 eV. After doping with cerium corresponding to the decrease of zirconium content, the binding energy of Cu $2p_{3/2}$ shifts slightly to the higher value, confirming that some Cu^+ is oxidized to Cu^{2+} . Zr 3d spectra (Figure 3B) of the catalysts exhibit doublets corresponding to Zr $3d_{3/2}$ at about 184.7 eV and Zr $3d_{5/2}$ at about 182.3 eV. The binding energy of Zr $3d_{5/2}$ in the catalyst is higher than that of zirconium metal (180.0 eV), but lower than that of ZrO_2 (182.4 eV) detected by our previous work (Bin et al., 2013), which might be caused by strong interactions at the ZSM-5 surface involving charge transfer from copper and cerium to zirconium.

The complex spectrum of Ce 3d is decomposed into eight components with the assignment defined in Figure 3C. The two sets of spin-orbital multiplets, corresponding to the $3d_{3/2}$ and $3d_{5/2}$ contributions, are labeled as u and v , respectively (Zhang et al., 2004). The four intense components v (882.8 eV), u (901.2 eV), v_3 (898.5 eV), and u_3 (916.9 eV), as well as the two weaker components v_2 (888.9 eV) and u_2 (908.4 eV), can be attributed to different Ce 4f electron configuration in the final states of the Ce^{4+} species. The v_1 (884.5 eV) and u_1 (903.2 eV) components correspond to one of the two possible electron configurations of the final state of the Ce^{3+} species (Katta et al., 2010; Su et al., 2014). The O 1s XPS spectra of the catalysts (Figure 3D) show three deconvolution peaks. The peak at the binding energy of 532.0 eV may be assigned to regular lattice oxygen bonded to silicon and aluminum as SiO_2 and Al_2O_3 from the ZSM-5 zeolite structure (O_Z). The peak at the binding energy of 533.2 eV corresponds to the presence of chemisorbed oxygen (O_A) and weakly hydroxyl/carbonates species. The shoulder peak at about 530.0 eV corresponds to characteristic lattice oxygen (O_L) bound to copper, cerium, and zirconium cations.

Figure 3. XPS narrow spectra of Cu 2p (A), Zr 3d (B), Ce 3d (C), and O 1s (D) from $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts: (a) CuZr_1/Z , (b) $\text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z}$, (c) $\text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z}$, (d) $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$, and (e) CuCe_1/Z . Crude line: original data; smooth line: fitting line.

Elemental compositions are calculated from the areas of Cu 2p, Ce 3d, and O 1s peaks. In particular, the concentration of Ce^{3+} and Ce^{4+} cations of the catalysts can be estimated as Eqs. (1) and (2) (Konysheva and Francis, 2013), where the $[\text{Ce}^{3+}]$ and $[\text{Ce}^{4+}]$ stand for the sums of the integrated peak areas related to their XPS signals respectively:

$$[\text{Ce}^{3+}] = v_1 + u_1 \quad (1)$$

$$[\text{Ce}^{4+}] = v + v_2 + v_3 + u + u_2 + u_3 \quad (2)$$

Table 1. Surface compositions of $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts derived from XPS analysis.

Sample	Cu/Si (atomic)		Ce/Si (atomic)		Zr/Si (atomic)		$\text{Cu}^{2+}/\text{Cu}^+$	$\text{Ce}^{3+}/\text{Ce}^{4+}$	$\text{O}_L/(\text{Cu}+\text{Ce}+\text{Zr})$
	XPS	AAS	XPS	AAS	XPS	AAS			
CuZr_1/Z	0.128	0.026	0	0	0.349	0.029	1.17	—	1.17
$\text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z}$	0.150	0.025	0.022	0.007	0.280	0.021	1.19	0.195	1.36
$\text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z}$	0.240	0.024	0.066	0.016	0.342	0.017	1.36	0.250	1.52
$\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$	0.272	0.026	0.106	0.024	0.148	0.009	3.35	0.279	1.96
CuCe_1/Z	0.253	0.024	0.173	0.030	0	0	1.95	0.255	2.43

As shown in Table 1, the Cu/Si, Ce/Si, and Zr/Si ratios detected by XPS are higher than those obtained from atomic absorption spectroscopy, indicating that the copper, cerium, and zirconium are enriched on the surface of ZSM-5 grains since XPS as a surface technique preferentially detects species with a sampling depth of 3–10 nm. Although the Cu/Si ratio of the bulk is maintained at about 0.025, the surface atomic ratio of Cu/Si ratio increases with cerium content, reaching the maximum of 0.272 for the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$. It is obvious that the enriched copper ions may interact with cerium ions to cover the ZSM-5 grains. A lower Cu/Si ratio (0.253) is obtained for the CuCe_1/Z as a result of the overmuch cerium ions aggregated to form ceria, which has been validated by the XRD analyses. With the cerium content increasing, both $\text{Cu}^{2+}/\text{Cu}^+$ and $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratios increase simultaneously to 3.35 and 0.279 ($\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$), respectively. These results provide unambiguous evidence of existence of redox equilibrium of $\text{Cu}^+ + \text{Ce}^{4+} \leftrightarrow \text{Cu}^{2+} + \text{Ce}^{3+}$, which has been claimed to be the source of a synergistic interaction between copper and cerium species (Qi et al., 2012). It is evident from Table 1 that the cerium is mostly in a quadrivalence oxidation state, and a small quantity of Ce^{3+} co-existed. The enhancement of homogeneity of the Ce and Zr atoms can improve the valence change of the Ce ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$). The presence of Ce^{3+} may have partially arisen from the substitution of Ce^{4+} by Zr^{4+} or Cu^{2+} ions during the calcination process (Cai et al., 2014). The spontaneous transformation of Ce^{4+} ($r_{\text{Ce}^{4+}} = 0.97 \text{ \AA}$) ion to the larger Ce^{3+} ($r_{\text{Ce}^{3+}} = 1.10 \text{ \AA}$) could compensate for this lattice contraction. The binding energy of Zr 3d_{5/2} of the catalysts lower than that of ZrO_2 also proved the displacement of Zr^{4+} ions into the ceria lattice. Although no chemical shift is found in the O 1s feature with changing the cerium and zirconium composition, the $\text{O}_L/(\text{Cu} + \text{Ce} + \text{Zr})$ atomic ratios (Table 1) exceptionally enhance with the increase in cerium. This should be due to the presence of Ce^{3+} over a cerium-rich sample that favors the formation of charge imbalance, vacancies, and unsaturated chemical bonds on the sample surface, for which more chemisorbed oxygen or/and weakly bonded oxygen species would be brought (Wan et al., 2011).

H₂-TPR analysis

The redox behavior of the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts has been investigated by H_2 -TPR. As shown in Figure 4 and Table 2, the CuZr_1/Z catalyst exhibits four reductive peaks, denoted as α , β , γ , and δ . The α and β peaks are attributed to the reduction of well dispersed copper clusters and copper oxide nanocrystals, respectively. The γ peak, while quite weak, is ascribed to the reduction of Cu^{2+} ions of the bulk-type CuO particles. Some copper ions can be incorporated into the vacant sites of the cerium oxides to form a coordinated, oxygen-capped surface structure, corresponding to the δ peak (Deo and Wachs, 1994).

Figure 4. H₂-TPR profiles of the CuCe_xZr_{1-x}O_y/ZSM-5 catalysts: (a) CuZr₁/Z, (b) CuCe_{0.25}Zr_{0.75}/Z, (c) CuCe_{0.5}Zr_{0.5}/Z, (d) CuCe_{0.75}Zr_{0.25}/Z, and (e) CuCe₁/Z. Crude line: original data; smooth line: fitting line. Weight of catalyst: 200 mg; pretreatment: 20 vol% O₂ at 550°C for 30 min; measurement conditions: 5 vol% H₂ (50 mL/min), heating rate 10°C/min from 50–600°C.

Table 2. Redox properties of the CuCe_xZr_{1-x}O_y/ZSM-5 catalysts.

Sample	δ peak		α peak		β peak		ε peak		γ peak		Total uptake (μmol/g _{ca})
	T (°C)	H ₂ uptake (μmol/g _{ca})	T (°C)	H ₂ uptake (μmol/g _{ca})	T (°C)	H ₂ uptake (μmol/g _{ca})	T (°C)	H ₂ uptake (μmol/g _{ca})	T (°C)	H ₂ uptake (μmol/g _{ca})	
CuZr ₁ /Z	155	213	186	524	246	790	—	—	330	274	1801
CuCe _{0.25} Zr _{0.75} /Z	154	220	191	570	221	646	299	160	357	243	1839
CuCe _{0.5} Zr _{0.5} /Z	130	152	166	608	199	646	239	304	397	182	1892
CuCe _{0.75} Zr _{0.25} /Z	120	122	138	699	180	654	279	182	380	372	2029
CuCe ₁ /Z	129	198	154	654	197	532	316	388	401	167	1939

An effect of the Ce/Zr ratio on the H₂-TPR profiles can be obviously discerned. The temperatures of δ, α, and β peaks decrease from 155°C, 186°C, and 246°C for the CuZr₁/Z to 120°C, 138°C, and 180°C for the CuCe_{0.75}Zr_{0.25}/Z, respectively, probably because the copper oxide entity disperses well. Compared with the CuCe_{0.75}Zr_{0.25}/Z, however, the CuCe₁/Z catalyst shows higher temperatures of δ, α, and β peaks, namely 129°C, 154°C, and 197°C, respectively. When the cerium has been added, a new reduction peak ε appears at about 299°C (CuCe_{0.25}Zr_{0.75}/Z), assigned to the reduction of cerium oxide clusters. This

peak shifting toward high temperatures can associate with the cerium clusters aggregated with cerium content.

The total amount of H_2 consumed can be observed in Table 2. As expected, the H_2 uptake increases from 1801 $\mu\text{mol/g}_{\text{ca}}$ for the CuZr_1/Z to 2029 $\mu\text{mol/g}_{\text{ca}}$ for the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ with increasing the cerium loading, since the hydrogen uptake occurring not only attributes to the copper reduction but also ascribes to a partial reduction of the cerium surface for the cerium-containing catalysts at relatively low temperatures. The exception of this trend is the CuCe_1/Z catalyst. The ceria formed over the CuCe_1/Z catalyst results in the reduction not extended deep into the bulk of ceria crystalline, but confined to its surface, thus leading to a lower H_2 consumption than that of the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ catalyst.

O_2 -TPD and CO-TPD analyses

Besides redox behavior of copper and cerium species, the state of O species and their quantities are of also importance for the CO oxidation. This can be probed by the thermal desorption spectra of oxygen as illustrated in Figure 5, revealing the presence of $\alpha\text{-O}_2$, i.e., mobile oxygen, that is physically adsorbed in the reversible molecular form at 198–222°C; $\beta\text{-O}_2$ chemically adsorbed on the copper oxides at 258–277°C where copper cations are apt to increase their degree of oxidation and hence adsorb oxygen molecules or atoms with electrons; $\gamma\text{-O}_2$ centered at 332–355°C originating from the anion vacancies created as a result of mixed oxides over ZSM-5 surface, in which dispersed transition metal cations in low oxidation states have many centers capable of donating electrons; $\delta\text{-O}_2$ centered at 553–609°C associated with the release of the surface and bulk lattice oxygen bonded to matrix metal ions (Bielński and Haber, 1979; Zhang et al., 2010; Zhu et al., 2007).

Figure 5. O_2 -TPD profiles of the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts: (a) CuZr_1/Z , (b) $\text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z}$, (c) $\text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z}$, (d) $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$, and (e) CuCe_1/Z . Crude line: original data; smooth line: fitting line. Weight of catalyst: 200 mg; measurement conditions: O_2 (30 ml/min) saturation in 1 h, heating rate 10°C/min to 900°C .

The O₂-TPD profiles of all catalysts appear quite similar, and quantification of the deconvoluted peaks of the different desorbed oxygen is summarized in Table 3. The peak temperature of the α -, β -, γ -, and δ -O₂ is far higher than the temperature at which catalytic reaction started (TPO process of CO will be presented in the next section). In fact, the O₂ desorption threshold temperature is practically coincident to the temperature at which CO conversion became complete. Upon the addition of cerium corresponding to the decrease of zirconium content, all of the desorption peaks shift moderately to low regions and peak intensities increase. Compared with the other five catalysts, the CuCe_{0.75}Zr_{0.25}/Z catalyst shows the highest adsorption capacity of α -, β -, γ -, and δ -O₂ species. Here, the lower peak temperature implies the higher ability of supplying oxygen centers and the larger peak area indicates the more supplying oxygen centers. Such high adsorption capacity of oxygen obtained for the CuCe_{0.75}Zr_{0.25}/Z may arise from the copper surface enrichment and much Ce³⁺ over cerium-rich sample favoring the formation of oxygen vacancies. Such effects of cerium doping have been exemplified by the XPS studies.

Figure 6 displays the CO-TPD spectra of adsorbed CO on the CuCe_xZr_{1-x}O_y/ZSM-5 catalysts. The profiles of all catalysts exhibit three desorption peaks at about 135°C (α peak), 195°C (β peak), and 290°C (γ peak), respectively. The α peaks are mostly attributed to the desorption of weak physical adsorption of CO. This sort of adsorption cannot activate the CO molecule and thus has little contribution for the CO oxidation. The β and γ peaks at higher temperatures would arise from the middle intensive and strong CO adsorption (Wang et al., 2008). The in-situ DRIFT study described in the “In-situ DRIFT analysis” section confirms that CO is mainly adsorbed chemically on the catalyst surface to form carbonyls and carbonates and the former have a lower thermal stability than the latter. As such, the β peaks in this study can be ascribed to the carbonyls while the γ peaks can be associated with the carbonates. The CO molecules tend to be chemisorbed on Cu sites instead of Ce sites since the d-orbitals of Cu⁺ and Cu²⁺ are completely or nearly full of electrons, respectively, prone to establish strong bonding to CO. By contrast, the Ce³⁺ and Ce⁴⁺, with the outer shell electron distributions of 4f1 and 5s2 4d10 5p6, respectively, are difficult to offer electrons from d-orbitals to the anti-bonding π -orbitals. Suitable cerium addition not only leads to total CO adsorption increasing but the β peak shifting towards high temperature. Obviously, copper surface dispersion and enrichment induced by cerium addition would favor the CO adsorption. The β peak shifting towards

Table 3. O₂-TPD data from CuCe_xZr_{1-x}O_y/ZSM-5 catalysts.

Sample	α -O ₂		β -O ₂		β -O ₂		γ -O ₂		Total O ₂ adsorbed ($\mu\text{mol/g}_{\text{ca}}$)
	T (°C)	O ₂ adsorbed ($\mu\text{mol/g}_{\text{ca}}$)	T (°C)	O ₂ adsorbed ($\mu\text{mol/g}_{\text{ca}}$)	T (°C)	O ₂ adsorbed ($\mu\text{mol/g}_{\text{ca}}$)	T (°C)	O ₂ adsorbed ($\mu\text{mol/g}_{\text{ca}}$)	
CuZr ₁ /Z	212	16.4	260	13.1	332	5.48	609	9.67	44.7
CuCe _{0.25} Zr _{0.75} /Z	198	19.1	246	20.9	342	7.96	571	17.1	65.1
CuCe _{0.5} Zr _{0.5} /Z	213	16.7	261	18.3	349	11.5	566	25.7	72.2
CuCe _{0.75} Zr _{0.25} /Z	211	18.4	258	27.3	337	13.2	553	33.6	92.5
CuCe ₁ /Z	222	16.4	277	6.15	355	4.26	599	9.09	35.9

Figure 6. CO-TPD profiles of the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts: (a) CuZr_1/Z , (b) $\text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z}$, (c) $\text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z}$, (d) $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$, and (e) CuCe_1/Z . Crude line: original data; smooth line: fitting line. Weight of catalyst: 200 mg; measurement conditions: CO (30 ml/min) saturation in 1 h, heating rate $10^\circ\text{C}/\text{min}$ to 500°C .

high temperature validates the formation of strongly adsorbed CO. It is probable that the π^* CO anti-bonding orbitals filling by d electrons of Cu ions are enhanced, thus leading to a distinct weakening of the C–O bond. Based upon the CO-TPD analysis, the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ catalyst is more favorable for the adsorption/activation of CO molecules than others, and the amount of strongly adsorbed CO-species increases correspondingly. Moreover, the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ possesses excellent redox capacity (detected by H_2 -TPR) and adsorption/activation properties for O species (measured by O_2 -TPD). Hence, the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ catalyst will be expected considerably to obtain the higher rate of CO oxidation.

Temperature-programmed oxidation process of carbon monoxide

The results of the temperature-programmed oxidation process of CO for selected catalysts are shown in Figure 7. Solid lines (with the filled symbols) illustrate the changes of CO conversion recorded during temperature increase, while dashed lines (with open symbols) show conversions recorded during temperature decrease. Upon heating conditions, the CuZr_1/Z catalyst shows a slow induction process that begins at 283°C and then continues, at a relatively slow rate until 327°C . Because the CO oxidation is highly exothermic, it generates a local hot spot-type overheating of the active centers on the catalyst, resulting from the liberation of excessive heat (Biabani-Ravandi et al., 2013). When the oxidation rate is fast enough to induce a strong increase of the local temperature, the increase in exothermic heat flux from the reaction exceeds the increase in heat loss flux, and then the catalytic light-off phenomenon propagates, leading to a remarkable thermal runaway.

Upon the cooling feeding, the furnace temperature is allowed to descend. Notably, the 100% CO conversion can be consistently maintained even after the heating is stopped and

Figure 7. Temperature-programmed oxidation of 10 vol% CO + 15 vol% O₂/N₂ over the CuCe_xZr_{1-x}O_y/ZSM-5 catalysts. Catalyst weight = 240 mg; gas flow = 0.5 l/min; solid line: heating process; dashed line: cooling process.

the controlled temperature remains at room temperature. At that time, heat released from chemical reactions on the catalyst surface is removed from the active sites to the surrounding support material and the gas phase by convection, conduction, and radiation. Even if the heat is rapidly removed from the active sites, the fast mass and heat transfer on the gas–solid phase interface enhances the temperature gradients between the active sites and the support material so that such a self-sustained combustion can be well maintained. It is clear that the activity of the cerium-containing catalysts is much higher than that of the CuZr₁/Z. When the cerium content increases, the activity profile of the catalysts shifts toward low temperatures. The activity of catalysts for the CO self-sustained combustion follows the order: CuZr₁/Z < CuCe_{0.25}Zr_{0.75}/Z < CuCe_{0.5}Zr_{0.5}/Z < CuCe₁/Z < CuCe_{0.75}Zr_{0.25}Z. Further addition of cerium (CuCe₁/Z) decreases the activity of the catalyst. The reasons may be that the combination between cerium and zirconium to form mixed oxides increased copper dispersion when the cerium is added into catalysts, and those finely dispersed copper species were also enriched on the catalyst surface, which realize the best activity of the CuCe_{0.75}Zr_{0.25}/Z among the catalysts tested. Further addition of cerium (CuCe₁/Z) decreases the activity of the catalyst due to cerium ions aggregated to form ceria on the catalyst surface, which should decrease the mass transfer. The self-sustained combustion of CO over all of the catalysts tested can be maintained for 8 h with no deactivation of the catalyst.

Typical photographs of CO self-sustained combustion are presented in Figure 8. Except for the CuZr₁/Z catalyst, the luminous zones can be observed because of thermal radiation within the CuCe_{0.75}Zr_{0.25}Z and CuCe₁/Z catalyst beds, although the CO self-sustained combustion is achieved for the CuZr₁/Z, CuCe_{0.75}Zr_{0.25}/Z, and CuCe₁/Z catalysts. The luminous zone is located in the front of the CuCe_{0.75}Zr_{0.25}/Z catalyst bed while located in the middle of the CuCe₁/Z one, also validating that the CuCe_{0.75}Zr_{0.25}/Z exhibits a higher activity for the CO combustion, compared to the CuCe₁/Z one. It is probable for the

$\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ catalyst that most of CO can be oxidized rapidly due to the fast mass transfer and thus releases a lot of heat, enough to maintain the self-sustained combustion in the front of the catalyst bed, never needing to react along the gas flow.

Figure 9 shows oxidation of 1 vol%, 3 vol%, 5 vol%, 7 vol%, and 10 vol% CO over the best catalyst, i.e., $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$, with 15 vol% O_2 during heating and cooling processes. The CO self-sustained combustion can be achieved at the CO concentration of feed gas ≥ 5 vol%. When the CO concentration is set at 1 vol% and 3 vol%, the induction process of the heating lines maintain as a low reaction rate until the CO converts completely. CO_2 outlet concentration is also found to be increasing (not shown). This indicates the continuous conversion of CO to CO_2 . Upon the cooling feeding, the cooling lines of CO conversions are lower than the corresponding heating ones. The hysteresis formed may result from the local heating due to exothermic effect of reaction so that the controlled temperature can be decreased below the ignition temperature without influencing the reaction rate significantly. Because thermal effects at higher CO concentration are considerably higher than that at lower CO concentration, the CO concentration increasing promotes the enhancement of reaction rate. On one hand, the hysteresis in the case of 3 vol% CO is significantly broader than that of 1 vol% CO, essentially due to a shift of the cooling process from 195°C to 150°C. On the other hand, the induction process of heating lines is becoming ever shorter with the CO concentration increasing, viz. 167–199°C for 5 vol% CO, 161–187°C for 7 vol% CO, 138–169°C for 10 vol% CO, and hence, the heating lines shift towards low temperatures, corresponding to T_{50} for 241°C, 233°C, 201°C, 188°C, and 170°C for 1 vol%, 3 vol%, 5 vol%, 7 vol%, and 10 vol% CO, respectively.

Based on the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ catalyst, the effects of the catalyst bed length on CO oxidation have been evaluated at three different weights: 120 mg, 240 mg, and 480 mg using 10 vol% CO + 15 vol% O_2/N_2 with the gas flow = 0.5 L/min, corresponding to the GHSV (gas hourly space velocity): 120,000 h^{-1} , 60,000 h^{-1} , and 30,000 h^{-1} , respectively. Upon decreasing the catalyst weight from 480 mg to 120 mg, the T_{50} increases from 154°C to 194°C (Figure 10). The effects of the flow rate on CO oxidation have also been tested under the aforesaid gas component conditions, with the experimental results indicating that the higher flow rates lead to the heating lines shifting towards lower temperatures (Figure 11). The T_{50} (the temperature at which 50% conversion was reached) is achieved at 104°C, 201°C, 209°C, and 219°C when the flow rate is set at 0.25 l/min, 0.5 l/min, 0.75 l/min, and 1.0 l/min, respectively. When the length of the catalyst bed or flow rate enhances,

Figure 8. The CO self-sustained combustion at room temperature promoted by the CuZr_1/Z (A), $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ (B), and CuCe_1/Z (C) catalysts.

Figure 9. Temperature-programmed oxidation of 1 vol%, 3 vol%, 5 vol%, 7 vol%, 10 vol% CO + 15 vol% O₂/N₂ (1 vol% + 15 vol% O₂ + 40 vol% CO₂/N₂) over the CuCe_{0.75}Zr_{0.25}/Z catalyst. Catalyst weight = 240 mg; Gas flow = 0.5 l/min; solid line: heating process; dashed line: cooling process.

CO and O₂ molecules would have sufficient time to be adsorbed on the surface active sites and move out as the products from the pores of the catalyst. In this case, the diffusion would release the surface active sites and make them be able to adsorb more reactants molecules in the next time, thus raising the CO conversion.

Figure 12 describes the effect of O₂ inlet concentration on the CO self-sustained combustion behavior of the CuCe_{0.75}Zr_{0.25}/Z catalyst at 10 vol% CO concentration. The O₂ concentration in the reaction gas mixture is varied from 3 vol% to 15 vol%. When the O₂ concentration is set at 3 vol% and 4 vol%, respectively, only about 60% and 80% CO conversion can be achieved due to complete consumption of the oxygen in feed, which is also confirmed by monitoring the CO₂ outlet concentration simultaneously. The detected stoichiometry for this reaction involves the 2:1 mixture of CO and O₂ to produce CO₂ according to the basic reaction $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$. Further, 100% CO conversion can be obtained with both excess and stoichiometric O₂ concentrations. The heating lines shifting towards lower temperatures with the O₂ concentration increasing, prove that for the oxidation of CO into CO₂ over the CuCe_{0.75}Zr_{0.25}/Z catalyst, oxygen is required in a sufficient quantity. The effect of CO₂ inlet concentration on the CO oxidation is shown in Figure 13. When the CO₂ exists in the stream, the activity of CuCe_{0.75}Zr_{0.25}/Z is limited. The T₅₀ increases from 170°C to 232°C when the CO₂ concentration increases from 0 vol% to 75 vol%. In order to determine the effect of CO₂ chemical or thermal inhibition on CO conversion, we added a new experiment in the 1 vol% CO + 40 vol% CO₂ + 15 vol% O₂/N₂ atmosphere that is shown in Figure 9. It can be seen that such a profile shifts toward the high temperature direction, compared with that of 1 vol% CO + 15 vol% O₂/N₂, which testified the chemical inhibition of the gaseous CO₂. These results may be attributed to the competitive adsorption of CO and CO₂ on the catalyst surface and the formation of carbonates on the reductive catalyst that causes a reduction in active sites on the catalyst surface, which will be confirmed in in-situ DRIFT analysis.

Figure 10. Temperature-programmed oxidation of 10 vol% CO + 15 vol% O₂/N₂ over the CuCe_{0.75}Zr_{0.25}/Z catalyst with the catalyst weight of 120 mg, 240 mg, and 480 mg employed. Gas flow = 0.5 l/min; solid line: heating process; dashed line: cooling process.

Figure 11. Temperature-programmed oxidation of 10 vol% CO + 15 vol% O₂/N₂ over the CuCe_{0.75}Zr_{0.25}/Z catalyst with the gas flow of 0.25 l/min, 0.5 l/min, 0.75 l/min, and 1.0 l/min. Catalyst weight = 240 mg; solid line: heating process; dashed line: cooling process.

In-situ DRIFT analysis

In-situ DRIFT spectra recorded under the simple CO + O₂/He reaction stream are displayed in Figures 14 and 15. Bands formed under such a reactant stream are observed to be basically present in two distinct zones of wavenumbers in the spectra. The first zone in the 2400–2000 cm⁻¹ (Figure 14) displays the formation of gas phase CO₂, with the two rotational branches at 2364 cm⁻¹ and 2341 cm⁻¹, and carbonyls (Li et al., 2011b; Pollard et al., 2008). The strong bands at 2128 cm⁻¹ and 2169 cm⁻¹ are considered to be due to CO

Figure 12. Effects of O_2 concentration on CO self-sustained combustion over the $CuCe_{0.75}Zr_{0.25}/Z$ catalyst. Feed gas: 10 vol% CO + 3 vol%, 4 vol%, 5 vol%, 10 vol%, 15 vol% O_2/N_2 ; catalyst weight = 240 mg; gas flow = 0.5 l/min.

Figure 13. Effects of CO_2 concentration on CO self-sustained combustion over the $CuCe_{0.75}Zr_{0.25}/Z$ catalyst. Feed gas: 10 vol% CO + 15 vol% O_2 + 0 vol%, 30 vol%, 40 vol%, 75 vol% CO_2/N_2 ; catalyst weight = 240 mg; gas flow = 0.5 l/min.

adsorption at copper sites to form Cu^+ -carbonyls (Gott and Oyama, 2009). This chemisorption giving rise to Cu^+ -carbonyl species would take place when Cu^{2+} species (insert towards CO adsorption) are automatically reduced to Cu^+ in the starting catalysts, since the carbonyls adsorbed on Cu^{2+} yield bands of weakly held carbonyls at 2215 cm^{-1} (Gamarra and Martínez-Arias, 2009) from the $CuCe_{0.75}Zr_{0.25}/Z$ although its surface Cu^{2+}/Cu^+ ratio reaches 3.35 detected by XPS. However, the possibility that the catalyst starts from a partially reduced state (Cu^+) in the copper oxide component has also been discarded on the basis of XPS characterization from other groups (Hornés et al., 2009).

Figure 14. DRIFT spectra of 2400–2000 cm^{-1} on the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts after exposure to 10 vol% CO + 15 vol% O_2/N_2 at 150–300 °C. The reaction gas mixture was fed to the sample at a total flow rate of 30 ml/min.

Figure 15. DRIFT spectra of 1600–1200 cm^{-1} on the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts after exposure to 10 vol% CO + 15 vol% O_2/N_2 at 150–300 °C. The reaction gas mixture was fed to the sample at a total flow rate of 30 ml/min.

The presence of these Cu^+ -CO validates the existence of easy reduction copper in the catalysts, also in agreement with the results of the H_2 -TPR experiment. With increasing the temperature, the position of CO adsorption bands (2128 cm^{-1} and 2169 cm^{-1}) shows a slight shift to higher wavenumbers as well as their intensities becoming weak, because of the decreased CO coverage on the catalyst surface at higher temperatures. The weak band at 2104 cm^{-1} is assigned to the CO linearly adsorbed on Cu^0 (Manzoli et al., 2005), which is unstable and can be disregarded with the temperature increasing.

The other zone in the 1600–1200 cm^{-1} (Figure 15) exhibits adsorption peaks at 1581 cm^{-1} , 1515 cm^{-1} , 1471 cm^{-1} , 1406 cm^{-1} , 1324–1294 cm^{-1} , and 1258 cm^{-1} , which represent CO adsorption on the catalyst surface, forming bidentate carbonates (1584 cm^{-1} and 1324–1294 cm^{-1}), monodentate carbonates (1515 cm^{-1} and 1471 cm^{-1}), carboxylate (1406 cm^{-1}), and bicarbonate (1258 cm^{-1} ; Tseng et al., 2009). The formation of surface carbonate complexes involves adsorption of CO molecules in coordinative unsaturated

Lewis acid-based pair sites ($\text{Cu}^{n+}\text{-O}^{2-}$; Pokrovski et al., 2001). Considering the literature data (Tankov et al., 2012), the formation of bicarbonates includes a hydrogen bond between the protons in the Brønsted acid-based centers of alumina in ZSM-5 with an oxygen atom originating in the carbonates already existing on the copper sites. When the temperature is raised from 150°C to 300°C, the intensities of CO_2 , bicarbonate, carboxylate, bidentate, and monodentate carbonates intensify significantly, while the intensities of CO rapidly fall. These behaviors can be explained by the fact that the $\text{Cu}^{n+}\text{-CO}$ complexes have a lower thermal stability than that of bicarbonate, carboxylate, and carbonates. In this case, the $\text{Cu}^+\text{-carbonyls}$ complexes are easily converted to CO_2 due to its weaker adsorption to enhance CO oxidation, followed by decomposition of bicarbonate, carboxylate, and carbonates. The CO_2 that is forming and then adsorbed on the catalyst surface can occupy the adsorption sites of CO, increase the reduction energy of copper oxides, and inhibit the formation rate of Cu^+ species (Zou et al., 2009), which can be the information relevant to explain the inhibition of the CO oxidation activities induced by the presence of gaseous CO_2 (Figure 13). Concerning the differences among in-situ DRIFT spectra of the CuZr_1/Z , $\text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z}$, and $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$, the lower intensities of $\text{Cu}^{n+}\text{-CO}$ and carbonate species together with the higher intensities of CO_2 suggests the faster reaction rate obtained for the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$.

Conclusions

The present study highlights the effects of Ce/Zr ratio over the $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts on the low-temperature activity of CO oxidation. It is found that the activity of the cerium-containing catalysts is much higher than that of the CuZr_1/Z . The activity of the catalysts for the CO self-sustained combustion follows the order: $\text{CuZr}_1/\text{Z} < \text{CuCe}_{0.25}\text{Zr}_{0.75}/\text{Z} < \text{CuCe}_{0.5}\text{Zr}_{0.5}/\text{Z} < \text{CuCe}_1/\text{Z} < \text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$. The in-situ DRIFT study suggests that the CO oxidation over $\text{CuCe}_x\text{Zr}_{1-x}\text{O}_y/\text{ZSM-5}$ catalysts mainly follows the Mars–van Krevelen mechanism. CO is preferentially adsorbed on copper sites to yield $\text{Cu}^+\text{-carbonyls}$ along with a copper oxide reduction process. Due to its low thermal stability, the $\text{Cu}^+\text{-carbonyls}$ react easily with the neighboring lattice oxygen provided by the cerium-zirconium mixed oxides to produce gaseous CO_2 release. CO is secondly adsorbed on the surface activated oxygen of copper sites to produce bicarbonate, carboxylate, and carbonates. Further decomposition of carbonates to CO_2 involves the uptake of the activated oxygen and simultaneous reduction of Cu^{2+} to Cu^+ . The resulting oxygen vacancies are refilled rapidly and irreversibly by oxygen from the gas phase. Appropriate addition of cerium increases the activity of catalysts for the following reasons. First, the combination between cerium and zirconium to form mixed oxides on the ZSM-5 support increases copper dispersion and inhibits copper crystallization, according to the UV–vis DR results. The finely dispersed copper species are enriched on the catalyst surface (detected by XPS), which is beneficial to the CO adsorption and activation. Second, the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ possesses excellent redox capacity (detected by $\text{H}_2\text{-TPR}$) due to partial copper ions incorporated into cerium oxides and adsorption/activation properties for O species (measured by $\text{O}_2\text{-TPD}$). Hence, the $\text{CuCe}_{0.75}\text{Zr}_{0.25}/\text{Z}$ catalyst obtains the higher rate of CO oxidation. Third, the enhancement of homogeneity of the Ce and Zr atoms can improve the valence change of $\text{Ce}^{4+} \rightleftharpoons \text{Ce}^{3+}$, and the redox couple $\text{Ce}^{4+}/\text{Ce}^{3+}$ formed facilitates oxygen transport. In this case, even if the heat is rapidly removed from the

active sites, the fast mass and heat transfer on the gas–solid phase interface enhance the temperature gradients between the active sites and the support material, leading to induce a self-sustained combustion of CO at the lower temperature than that of CuZr₁/Z.

Funding

The authors gratefully acknowledge the financial support from the National Key Research and Development Program of China (2016YFB0601402).

References

- Aghalayam, P., Park, Y.K., and Vlachos, D.G. 2000. A detailed surface reaction mechanism for CO oxidation on Pt. *Proc. Combust. Inst.*, **28**, 1331–1339.
- Alayon, E.M.C., Singh, J., Nachtegaal, M., Harfouche, M., and Van Bokhoven, J.A. 2009. On highly active partially oxidized platinum in carbon monoxide oxidation over supported platinum catalysts. *J. Catal.*, **263**(2), 228–238.
- Biabani-Ravandi, A., Rezaei, M., and Fattah, Z. 2013. Low-temperature CO oxidation over nano-sized Fe–Co mixed oxide catalysts: Effect of calcination temperature and operational conditions. *Chem. Eng. Sci.*, **94**, 237–244.
- Bielński, A., and Haber, J. 1979. Oxygen in catalysis on transition metal oxides. *Catal. Rev. Sci. Eng.*, **19**, 1–41.
- Bin, F., Song, C.L., Lv, G., Song, J.O., Wang, K.P., and Li, X.D. 2013. Soot low-temperature combustion on Cu–Zr/ZSM-5 catalysts in O₂/He and NO/O₂/He atmospheres. *Proc. Combust. Inst.*, **34**(2), 2303–2311.
- Bin, F., Wei, X.L., Li, B., and Hui, K.S. 2015. Self-sustained combustion of carbon monoxide promoted by the Cu–Ce/ZSM-5 catalyst in CO/O₂/N₂ atmosphere. *Appl. Catal., B*, **162**, 282–288.
- Cai, W., Zhong, Q., Zhao, W., and Bu, Y. 2014. Focus on the modified Ce_xZr_{1–x}O₂ with the rigid benzene-muti-carboxylate ligands and its catalysis in oxidation of NO. *Appl. Catal., B*, 158–159, 258–268.
- Deo, G., and Wachs, I. E. 1994. Reactivity of supported vanadium oxide catalysts: The partial oxidation of methanol. *J. Catal.*, **146**(2), 323–334.
- Gamarra, D., and Martínez-Arias, A. 2009. Preferential oxidation of CO in rich H₂ over CuO/CeO₂: Operando-DRIFTS analysis of deactivating effect of CO₂ and H₂O. *J. Catal.*, **263**(1), 189–195.
- Gott, T., and Oyama, S.T. 2009. A general method for determining the role of spectroscopically observed species in reaction mechanisms: Analysis of coverage transients (ACT). *J. Catal.*, **263**, 359–371.
- Hornés, A., Bera, P., Cámara, A.L., Gamarra, D., and Munuera, G. 2009. CO-TPR-DRIFTS-MS in situ study of CuO/Ce_{1–x}Tb_xO_{2–y} ($x = 0, 0.2$ and 0.5) catalysts: Support effects on redox properties and CO oxidation catalysis. *J. Catal.*, **268**(2), 367–375.
- Katta, L., Sudarsanam, P., Thirumurthulu, G., and Reddy, B.M. 2010. Doped nanosized ceria solid solutions for low temperature soot oxidation: Zirconium versus lanthanum promoters. *Appl. Catal., B*, **101**, 101–108.
- Kolobova, E., Pestryakov, A., Mamontov, G., Kotolevich, Y., Bogdanchikov, N., Farias, M., Vosmerikov, A., Vosmerikov, L., and Cortes Corberan, V. 2017. Low-temperature CO oxidation on Ag/ZSM-5 catalysts: Influence of Si/Al ratio and redox pretreatments on formation of silver active sites. *Fuel*, **188**, 121–131.
- Konyshva, E.Y., and Francis, S.M. 2013. Identification of surface composition and chemical states in composites comprised of phases with fluorite and perovskite structures by X-ray photoelectron spectroscopy. *Appl. Surf. Sci.*, **268**, 278–287.
- Laguna, O.H., Pérez, A., Centeno, M.A., and Odriozola, J.A. 2015. Synergy between gold and oxygen vacancies in gold supported on Zr-doped ceria catalysts for the CO oxidation. *Appl. Catal., B*, **176–177**, 385–395.

- Landi, G., Barbato, P.S., Benedetto, A.D., Pirone, R., and Russo, G. 2013. High pressure kinetics of CH₄, CO and H₂ combustion over LaMnO₃ catalyst. *Appl. Catal., B*, **134–135**, 110–122.
- Li, J., Han, Y.X., Zhu, Y.H., and Zhou, R.X. 2011a. Purification of hydrogen from carbon monoxide for fuel cell application over modified mesoporous CuO–CeO₂ catalysts. *Appl. Catal., B*, **109**, 72–80.
- Li, S., Wei, X.L., and Yu, L.X. 2011b. Numerical simulation of off-gas formation during top-blown oxygen converter steelmaking. *Fuel*, **90**(4), 1350–1360.
- Liang, C.X., Li, X.Y., Qu, Z.P., Tade, M., and Liu, S.M. 2012. The role of copper species on Cu/γ-Al₂O₃ catalysts for NH₃–SCO reaction. *Appl. Surf. Sci.*, **258**(8), 3738–3743.
- Liu, L.J., Yao, Z.J., Liu, B., and Dong, L. 2010. Correlation of structural characteristics with catalytic performance of CuO/Ce_xZr_{1–x}O₂ catalysts for NO reduction by CO. *J. Catal.*, **275**(1), 45–60.
- Lukac, J., Klementova, M., Bezduka, P., Bakardjieva, S., Subrt, J., Saztma, L., Bastl, Z., and Jirkovsky, J. 2007. Influence of Zr as TiO₂ doping ion on photocatalytic degradation of 4-chlorophenol. *Appl. Catal., B*, **74**, 83–91.
- Lundgren, J., Ekblom, T., Hultberg, C., Larsson, M., Grip, C.E., Nilsson, L., and Tunå, P. 2013. Methanol production from steel-work off-gases and biomass based synthesis gas. *Appl. Energy*, **112**, 431–439.
- Manzoli, M., Monte, R.D., Boccuzzi, F., Coluccia, S., and Kašpar, J. 2005. CO oxidation over CuO_x–CeO₂–ZrO₂ catalysts: Transient behaviour and role of copper clusters in contact with ceria. *Appl. Catal., B*, **61**, 192–205.
- Mhadeshwar, A.B., and Vlachos, D.G. 2005. Hierarchical, multiscale surface reaction mechanism development: CO and H₂ oxidation, water–gas shift, and preferential oxidation of CO on Rh. *J. Catal.*, **234**, 48–63.
- Moretti, E., Storaro, L., Talon, A., Lenarda, M., Riello, P., Frattini, R., De Yuso, M.V.M., Jiménez-López, A., Rodríguez-Castellón, E., Ternero, F., Caballero, A., and Holgado, J.P. 2011. Effect of thermal treatments on the catalytic behaviour in the CO preferential oxidation of a CuO–CeO₂–ZrO₂ catalyst with a flower-like morphology. *Appl. Catal., B*, **102**, 627–637.
- Moretti, E., Storaro, L., Talon, A., Riello, P., Molina, A.I., and Rodríguez-Castellón, E. 2015. 3-D flower like Ce–Zr–Cu mixed oxide systems in the CO preferential oxidation (CO-PROX): Effect of catalyst composition. *Appl. Catal., B*, **168–169**, 385–395.
- Pokrovski, K., Lung, K.T., and Bell, A.T. 2001. Investigation of CO and CO₂ adsorption on tetragonal and monoclinic zirconia. *Langmuir*, **17**(14), 4297–4303.
- Pollard, M.J., Weinstock, B.A., Bitterwolf, T.E., Griffiths, P.R., Newbery, A.P., and Paine, J.B. 2008. A mechanistic study of the low-temperature conversion of carbon monoxide to carbon dioxide over a cobalt oxide catalyst. *J. Catal.*, **254**(2), 218–225.
- Postole, G., Chowdhury, B., Karmakar, B., Pinki, K., Banerji, J., and Auroux, A. 2010. Knoevenagel condensation reaction over acid–base bifunctional nanocrystalline Ce_xZr_{1–x}O₂ solid solutions. *J. Catal.*, **269**(1), 110–121.
- Praliaud, H., Mikhailenko, S., Chajar, Z., and Primet, M. 1998. Surface and bulk properties of Cu–ZSM-5 and Cu/Al₂O₃ solids during redox treatments. Correlation with the selective reduction of nitric oxide by hydrocarbons. *Appl. Catal., B*, **16**, 359–374.
- Qi, L., Yu, Q., Dai, Y., Tang, C., Liu, L., Zhang, H., Gao, F., and Dong, L. 2012. Influence of cerium precursors on the structure and reducibility of mesoporous CuO–CeO₂ catalysts for CO oxidation. *Appl. Catal., B*, 119–120, 308–320.
- Shao, Y.M., Zhou, M.C., Chen, Y.R., Zhao, Q., and Zhao, S. 2014. BOF endpoint prediction based on the flame radiation by hybrid SVC and SVR modeling. *Optik*, **125**(11), 2491–2496.
- Sinha, A.K., and Suzuki, K. 2005. Preparation and characterization of novel mesoporous ceria-titania. *J. Phys. Chem. B*, **109**(5), 1708–1714.
- Su, Y.F., Tang, Z.C., Han, W.L., Zhang, P., Song, Y., and Lu, G.X. 2014. Influence of the pore structure of CeO₂ supports on the surface texture and catalytic activity for CO oxidation. *Cryst. Eng. Commun.*, **16**(24), 5189–5197.
- Tankov, I., Cassinelli, W.H., Bueno, J.M.C., Arishtirova, K., and Damyanova, S. 2012. DRIFTS study of CO adsorption on praseodymium modified Pt/Al₂O₃. *Appl. Surf. Sci.*, **259**, 831–839.

- Tseng, C.H., Yang, T.C.K., Wu, H.E., and Chiang, H.C. 2009. Catalysis of oxidation of carbon monoxide on supported gold nanoparticle. *J. Hazard. Mater.*, **166**, 686–694.
- Veser, G., Ziauddin, M., and Schmidt, L.D. 1999. Ignition in alkane oxidation on noble-metal catalysts. *Catal. Today*, **47**(1–4), 219–228.
- Wan, Q., Duan, L., He, K.B., and Li, J.H. 2011. Removal of gaseous elemental mercury over a $\text{CeO}_2\text{-WO}_3/\text{TiO}_2$ nanocomposite in simulated coal-fired flue gas. *Chem. Eng. J.*, **170**(2–3), 512–517.
- Wang, T., Ding, Y.J., Lv, Y., Zhu, H.J., and Lin, L.W. 2008. Influence of lanthanum on the performance of Zr-Co/activated carbon catalysts in Fischer-Tropsch synthesis. *J. Nat. Gas Chem.*, **17**(2), 153–158.
- Zhang, F., Wang, P., Koberstein, J., Khalid, S., and Chan, S.W. 2004. Cerium oxidation state in ceria nanoparticles studied with X-ray photoelectron spectroscopy and absorption near edge spectroscopy. *Surf. Sci.*, **563**(1–3), 74–82.
- Zhang, R.D., Teoh, W.Y., Amal, R., Chen, B.H., and Kaliaguine, S. 2010. Catalytic reduction of NO by CO over $\text{Cu/Ce}_x\text{Zr}_{1-x}\text{O}_2$ prepared by flame synthesis. *J. Catal.*, **272**(2), 210–219.
- Zhou, X.X., Chen, H.R., Cui, X.Z., Hua, Z.L., Chen, Y., Zhu, Y., Song, Y.D., Gong, Y., and Shi, J.L. 2013. A facile one-pot synthesis of hierarchically porous Cu (I)-ZSM-5 for radicals-involved oxidation of cyclohexane. *Appl. Catal., A*, **451**, 112–119.
- Zhu, L., Yu, J.J., and Wang, X.Z. 2007. Oxidation treatment of diesel soot particulate on $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$. *J. Hazard. Mater.*, **140**(1–2), 205–210.
- Zou, H.B., Chen, S.Z., Liu, Z.L., and Lin, W.M. 2009. DRIFTS study of Cu-Zr-Ce-O catalysts for selective CO oxidation. *Int. J. Hydrogen Energy*, **34**(23), 9324–9333.