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

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ABSTRACT
The self-sustained combustion of CO was studied over a series of CuCe$_{1-x}$Zr$_x$O$_y$/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: CuZr$_1$/Z < CuCe$_{0.25}$Zr$_{0.75}$/Z < CuCe$_{0.5}$Zr$_{0.5}$/Z < CuCe$_{1}$/Z < CuCe$_{0.75}$Zr$_{0.25}$/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 CuCe$_{0.75}$Zr$_{0.25}$/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 CuCe$_{1-x}$Zr$_x$O$_y$/ZSM-5 catalysts.

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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
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/Al$_2$O$_3$, Pt/TiO$_2$, and Pt/SiO$_2$ 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/O$_2$ 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/O$_2$ ratio of 1.0 for various N$_2$ 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$_x$Zr$_{1-x}$O$_2$ solid solution conduces to shape structural defects due to substitution of Ce$^{4+}$ by Zr$^{4+}$, thus further enhances the oxygen mobility through the lattice, redox property, and sintering-resistant of CeO$_2$ (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$_x$Zr$_{1-x}$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), H$_2$ temperature-programmed reduction (H$_2$-TPR), temperature-programmed desorption of CO/O$_2$ (CO/O$_2$-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 CuCe\(_x\)Zr\(_{1-x}\)O\(_y\)/ZSM-5 catalysts (\(x = 0, 0.25, 0.5, 0.75,\) and 1, denoted as CuCe\(_x\)Zr\(_{1-x}\)/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 CuCe\(_x\)Zr\(_{1-x}\)O\(_y\)/ZSM-5 catalysts was fixed at 2.0 wt%, and the molar ratio of Cu/(Ce+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 Ka radiation (40 kV, 200 mA, \(\lambda = 1.5418\) Å). Diffractometer data were acquired with a step size of 0.02° for 2\(\theta\) 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 Ka 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°C/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°C/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 CuCeₓZr₁₋ₓOₓ/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% O₂ and N₂ as balance. The effect of CO, O₂, and CO₂ 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% O₂; 0 vol%, 30 vol%, 40 vol%, and 75 vol% CO₂, 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, O₂, and CO₂ 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 θ = 7.9°, 8.8°, 23.1°, and 23.8° (PDF 44-0003), representing (011), (200), (051), and (033) 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 CuZr₁/Z, CuCe₀.₂₅Zr₀.₇₅/Z, CuCe₀.₅Zr₀.₅/Z, and CuCe₀.₇₅Zr₀.₂₅/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 ≤ 0.75. The presence of cubic CeO₂ (2θ = 28.2°, PDF = 34-0394) on the CuCe₁/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 CuZr₁/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 Cu²⁺ 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 Cu²⁺ 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 Cu²⁺ 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 CeO₂ at 285 nm, assigned to O²⁻–Ce⁴⁺ charge transfer transitions (Sinha...
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 in 358 nm, 389 nm, 450 nm, 451 nm, and 472 nm for CuZr\textsubscript{1}/Z, CuCe\textsubscript{0.25}Zr\textsubscript{0.75}/Z, CuCe\textsubscript{0.5}Zr\textsubscript{0.5}/Z, CuCe\textsubscript{0.75}Zr\textsubscript{0.25}/Z, and CuCe\textsubscript{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\textsubscript{1}/Z catalyst shows two main peaks that are attributed to Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2} at about 933.8 eV and 954.3 eV, respectively. Due to considerable asymmetry of the Cu
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_{5/2} at about 184.7 eV and Zr 3d_{3/2} 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^{2+} 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_{2}O_{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.
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 [Ce$^{3+}$] and [Ce$^{4+}$] stand for the sums of the integrated peak areas related to their XPS signals respectively:

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

$$[\text{Ce}^{4+}] = v + v_2 + v_3 + u + u_2 + u_3$$  \hspace{1cm} (2)

Figure 3. XPS narrow spectra of Cu 2p (A), Zr 3d (B), Ce 3d (C), and O 1s (D) from CuCe$_x$Zr$_{1-x}$O$_y$/ZSM-5 catalysts: (a) CuZr$_1$/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) CuCe$_1$/Z. Crude line: original data; smooth line: fitting line.
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 CuCe0.75Zr0.25/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 CuCe1/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 Cu2+/Cu+ and Ce3+/Ce4+ ratios increase simultaneously to 3.35 and 0.279 (CuCe0.75Zr0.25/Z), respectively. These results provide unambiguous evidence of existence of redox equilibrium of Cu+ + Ce4+ ↔ Cu2+ + Ce3+, 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 Ce3+ co-existed. The enhancement of homogeneity of the Ce and Zr atoms can improve the valence change of the Ce (Ce4+ → Ce3+). The presence of Ce3+ may have partially arisen from the substitution of Ce4+ by Zr4+ or Cu2+ ions during the calcination process (Cai et al., 2014). The spontaneous transformation of Ce4+ (rCe4+ = 0.97 Å) ion to the larger Ce3+ (rCe3+ = 1.10 Å) could compensate for this lattice contraction. The binding energy of Zr 3d5/2 of the catalysts lower than that of ZrO2 also proved the displacement of Zr4+ ions into the ceria lattice. Although no chemical shift is found in the O 1s feature with changing the cerium and zirconium composition, the O1/(Cu + Ce + Zr) atomic ratios (Table 1) exceptionally enhance with the increase in cerium. This should be due to the presence of Ce3+ 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 CuCe7Zr1-xOy/ZSM-5 catalysts has been investigated by H2-TPR. As shown in Figure 4 and Table 2, the CuZr1/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 minicrystals, respectively. The γ peak, while quite weak, is ascribed to the reduction of Cu2+ 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).
An effect of the Ce/Zr ratio on the $\text{H}_2$-TPR profiles can be obviously discerned. The temperatures of $\delta$, $\alpha$, and $\beta$ peaks decrease from 155°C, 186°C, and 246°C for the CuZr$_1$/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 CuCe$_1$/Z catalyst shows higher temperatures of $\delta$, $\alpha$, and $\beta$ peaks, namely 129°C, 154°C, and 197°C, respectively. When the cerium has been added, a new reduction peak $\epsilon$ appears at about 299°C (CuCe$_{0.25}$Zr$_{0.75}$/Z), assigned to the reduction of cerium oxide clusters. This

![Figure 4](image-url). $\text{H}_2$-TPR profiles of the CuCe$_x$Zr$_{1-x}$/ZSM-5 catalysts: (a) CuZr$_1$/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) CuCe$_1$/Z. Crude line: original data; smooth line: fitting line. Weight of catalyst: 200 mg; pretreatment: 20 vol% O$_2$ at 550°C for 30 min; measurement conditions: 5 vol% $\text{H}_2$ (50 mL/min), heating rate 10°C/min from 50–600°C.

| Sample          | $\delta$ peak | $\alpha$ peak | $\beta$ peak | $\epsilon$ peak | $\gamma$ peak | Total uptake |
|-----------------|---------------|---------------|--------------|-----------------|--------------|--------------|
|                 | T (°C)        | $\text{H}_2$ uptake (μmol/g$_{\text{cat}}$) | T (°C)        | $\text{H}_2$ uptake (μmol/g$_{\text{cat}}$) | T (°C)        | $\text{H}_2$ uptake (μmol/g$_{\text{cat}}$) | T (°C)        | $\text{H}_2$ uptake (μmol/g$_{\text{cat}}$) | T (°C)        | $\text{H}_2$ uptake (μmol/g$_{\text{cat}}$) |
| 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           | 1839          | |
| CuCe$_{0.5}$Zr$_{0.5}$/Z   | 130           | 152           | 166          | 608             | 199          | 646          | 239          | 304           | 1892          | |
| CuCe$_{0.75}$Zr$_{0.25}$/Z | 120           | 122           | 138          | 699             | 180          | 654          | 279          | 182           | 2029          | |
| CuCe$_1$/Z      | 129           | 198           | 154          | 654             | 197          | 532          | 316          | 388           | 1939          |
peak shifting toward high temperatures can associate with the cerium clusters aggregated with cerium content.

The total amount of $\text{H}_2$ consumed can be observed in Table 2. As expected, the $\text{H}_2$ 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 CuCe$_{0.75}$Zr$_{0.25}$/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 $\text{H}_2$ consumption than that of the CuCe$_{0.75}$Zr$_{0.25}$/Z catalyst.

**$\text{O}_2$-TPD and CO-TPD analyses**

Besides redox behavior of copper and cerium species, the state of $\text{O}$ 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. $\text{O}_2$-TPD profiles of the CuCe$_x$Zr$_{1-x}$/O$_y$/ZSM-5 catalysts: (a) CuZr$_1$/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) CuCe$_1$/Z. Crude line: original data; smooth line: fitting line. Weight of catalyst: 200 mg; measurement conditions: $\text{O}_2$ (30 ml/min) saturation in 1 h, heating rate 10°C/min to 900°C.](image-url)
The O$_2$-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-O$_2$ 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 O$_2$ 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-O$_2$ 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 Ce$^{3+}$ 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$_{x}$Zr$_{1-x}$/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 carboxyls 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 carboxyls 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 Cu$^{2+}$ are completely or nearly full of electrons, respectively, prone to establish strong bonding to CO. By contrast, the Ce$^{3+}$ and Ce$^{4+}$, 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

| Sample     | α-O$_2$| β$_1$-O$_2$| β$_2$-O$_2$| γ-O$_2$| Total O$_2$ adsorbed (μmol/g) |
|------------|--------|-----------|-----------|--------|-------------------------------|
| CuZr/ 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 |
high temperature validates the formation of strongly adsorbed CO. It is probable that the $\pi^*$ 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 CuCe$_{0.75}$Zr$_{0.25}$/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 CuCe$_{0.75}$Zr$_{0.25}$/Z possesses excellent redox capacity (detected by H$_2$-TPR) and adsorption/activation properties for O species (measured by O$_2$-TPD). Hence, the CuCe$_{0.75}$Zr$_{0.25}$/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
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 < CuCe0.25Zr0.75/Z < CuCe0.5Zr0.5/Z < CuCe1/Z < CuCe0.75Zr0.25/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 CuCe0.75Zr0.25/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 CuCe0.75Zr0.25/Z and CuCe1/Z catalyst beds, although the CO self-sustained combustion is achieved for the CuZr1/Z, CuCe0.75Zr0.25/Z, and CuCe1/Z catalysts. The luminous zone is located in the front of the CuCe0.75Zr0.25/Z catalyst bed while located in the middle of the CuCe1/Z one, also validating that the CuCe0.75Zr0.25/Z exhibits a higher activity for the CO combustion, compared to the CuCe1/Z one. It is probable for the
CuCe\textsubscript{0.75}Zr\textsubscript{0.25}/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., CuCe\textsubscript{0.75}Zr\textsubscript{0.25}/Z, with 15 vol% O\textsubscript{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\textsubscript{2} outlet concentration is also found to be increasing (not shown). This indicates the continuous conversion of CO to CO\textsubscript{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\textsubscript{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 CuCe\textsubscript{0.75}Zr\textsubscript{0.25}/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\textsubscript{2}/N\textsubscript{2} with the gas flow = 0.5 L/min, corresponding to the GHSV (gas hourly space velocity): 120,000 h\textsuperscript{-1}, 60,000 h\textsuperscript{-1}, and 30,000 h\textsuperscript{-1}, respectively. Upon decreasing the catalyst weight from 480 mg to 120 mg, the T\textsubscript{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\textsubscript{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,
CO and O$_2$ 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 O$_2$ 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 O$_2$ concentration in the reaction gas mixture is varied from 3 vol% to 15 vol%. When the O$_2$ 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 CO$_2$ outlet concentration simultaneously. The detected stoichiometry for this reaction involves the 2:1 mixture of CO and O$_2$ to produce CO$_2$ according to the basic reaction 2CO + O$_2$ → 2CO$_2$. Further, 100% CO conversion can be obtained with both excess and stoichiometric O$_2$ concentrations. The heating lines shifting towards lower temperatures with the O$_2$ concentration increasing, prove that for the oxidation of CO into CO$_2$ over the CuCe$_{0.75}$Zr$_{0.25}$/Z catalyst, oxygen is required in a sufficient quantity. The effect of CO$_2$ inlet concentration on the CO oxidation is shown in **Figure 13**. When the CO$_2$ exists in the stream, the activity of CuCe$_{0.75}$Zr$_{0.25}$/Z is limited. The T$_{50}$ increases from 170°C to 232°C when the CO$_2$ concentration increases from 0 vol% to 75 vol%. In order to determine the effect of CO$_2$ chemical or thermal inhibition on CO conversion, we added a new experiment in the 1 vol% CO + 40 vol% CO$_2$ + 15 vol% O$_2$/N$_2$ 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% O$_2$/N$_2$, which testified the chemical inhibition of the gaseous CO$_2$. These results may be attributed to the competitive adsorption of CO and CO$_2$ 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.
In-situ DRIFT analysis

In-situ DRIFT spectra recorded under the simple CO + O$_2$/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 CO$_2$, 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.
adsorption at copper sites to form Cu⁺-carbonyls (Gott and Oyama, 2009). This chemisorption giving rise to Cu⁺-carbonyl species would take place when Cu²⁺ species (insert towards CO adsorption) are automatically reduced to Cu⁺ in the starting catalysts, since the carbonyls adsorbed on Cu²⁺ yield bands of weakly held carbonyls at 2215 cm⁻¹ (Gamarra and Martínez-Arias, 2009) from the CuCe₀.₇₅Zr₀.₂₅/Z catalyst although its surface Cu²⁺/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 12. Effects of O₂ concentration on CO self-sustained combustion over the CuCe₀.₇₅Zr₀.₂₅/Z catalyst. Feed gas: 10 vol% CO + 3 vol%, 4 vol%, 5 vol%, 10 vol%, 15 vol% O₂/N₂; catalyst weight = 240 mg; gas flow = 0.5 l/min.

Figure 13. Effects of CO₂ concentration on CO self-sustained combustion over the CuCe₀.₇₅Zr₀.₂₅/Z catalyst. Feed gas: 10 vol% CO + 15 vol% O₂ + 0 vol%, 30 vol%, 40 vol%, 75 vol% CO₂/N₂; catalyst weight = 240 mg; gas flow = 0.5 l/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° (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 (Cu

\( ^{n+} \)-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 Cu

\( ^{n+} \)--CO complexes have a lower thermal stability than that of bicarbonate, carboxylate, and carbonates. In this case, the Cu

\( ^{+} \)-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

\( _1 /Z\), CuCe

\( _{0.5} \text{Zr}_{0.5} /Z\), and CuCe

\( _{0.75} \text{Zr}_{0.25} /Z\), the lower intensities of Cu

\( ^{n+} \)--CO and carbonate species together with the higher intensities of CO\(_2\) suggests the faster reaction rate obtained for the CuCe

\( _{0.75} \text{Zr}_{0.25} /Z\).

**Conclusions**

The present study highlights the effects of Ce/Zr ratio over the 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: CuZr

\( _1 /Z < \text{CuCe}_{0.25} \text{Zr}_{0.75} /Z < \text{CuCe}_{0.5} \text{Zr}_{0.5} /Z < \text{CuCe}_{1} /Z < \text{CuCe}_{0.75} \text{Zr}_{0.25} /Z\). The in-situ DRIFT study suggests that the CO oxidation over 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 Cu\(^+\)-carbonyls along with a copper oxide reduction process. Due to its low thermal stability, the Cu\(^+\)-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 CuCe

\( _{0.75} \text{Zr}_{0.25} /Z\) possesses excellent redox capacity (detected by H\(_2\)-TPR) due to partial copper ions incorporated into cerium oxides and adsorption/activation properties for O species (measured by O\(_2\)-TPD). Hence, the CuCe

\( _{0.75} \text{Zr}_{0.25} /Z\) 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 Ce

\( ^{4+} \to \text{Ce}^{3+}\), and the redox couple 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.

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