

CO oxidation over CuO catalysts supported on CeO₂-ZrO₂ prepared by microwave-assisted co-precipitation: The influence of CuO content

YANG Zhiqiang (杨志强), MAO Dongsen (毛东森)*, GUO Xiaoming (郭晓明), LU Guanzhong (卢冠忠)

(Research Institute of Applied Catalysis, School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China)

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Abstract: CeO₂-ZrO₂ mixed oxide (Ce_{0.6}Zr_{0.4}O₂) prepared by microwave-assisted heating co-precipitation was used as a support to prepare a series of CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts with various CuO contents (0 wt.%–15 wt.%) via the method of incipient-wetness impregnation. The obtained CuO/Ce_{0.6}Zr_{0.4}O₂ samples were characterized by N₂ adsorption, XRD, Raman, TEM and H₂-TPR technologies, and their catalytic activities for CO oxidation were investigated. The results showed that the activity of CuO/Ce_{0.6}Zr_{0.4}O₂ catalyst was strongly influenced by the content of CuO, and the catalyst with 10 wt.% CuO exhibited the best catalytic activity in CO oxidation, which could be attributed to the high dispersion and reducibility of CuO, and high oxygen vacancy concentration in the catalyst.

Keywords: cerium-zirconium mixed oxide; copper oxide; microwave heating; CO oxidation; rare earths

CuO/Ce_xZr_{1-x}O₂ catalyst, due to its high catalytic activity in CO oxidation, has been extensively investigated in recent years^[1–16]. Considering the fact that impregnation method possesses the merit of simplicity, convenience and high effectiveness, CuO/Ce_xZr_{1-x}O₂ catalysts are usually prepared by impregnating Cu precursor on Ce_xZr_{1-x}O₂ mixed oxide, followed by drying and calcining^[1–4,8,11,12]. Many studies have shown that the catalytic property of CuO/Ce_xZr_{1-x}O₂ for CO oxidation strongly depended on the preparation methodology of support Ce_xZr_{1-x}O₂. For example, Wang et al.^[8] found that for the CuO/Ce_{0.8}Zr_{0.2}O₂ catalyst, its catalytic activity with Ce_{0.8}Zr_{0.2}O₂ prepared by hydrothermal crystalline was obviously superior to that by co-precipitation. Recently, Zhu and co-workers^[12] reported the same result for CuO/Ce_{0.67}Zr_{0.33}O₂ catalyst. So far, many methods have been utilized to prepare the cerium-zirconium mixed oxides, including sol-gel, co-precipitation, hydrothermal synthesis, high-energy ball milling and many others. Among these methods, co-precipitation, which is considered to be a simple and convenient method, has been deeply researched and widely applied^[17–19]. Moreover, it was well illustrated that the surface area and thermal stability of cerium-zirconium mixed oxide could be enhanced by heating and refluxing the precursor prepared by co-precipitation^[20–22]. As is known to all, the microwave heating is basically different from the conventional heating wherein the heat generates internally through material-microwave interaction instead of originating from an external heating source. Since the microwave

heating has the advantages such as rapid and uniform heating, it was used recently by us to the heating and refluxing treatment of the precursor obtained by co-precipitation^[23]. The results showed that the Ce_{0.6}Zr_{0.4}O₂ sample prepared by microwave-assisted heating and refluxing had higher specific surface area and better redox ability than that prepared by conventional electric heating and refluxing^[23]. Moreover, the CuO species loaded on Ce_{0.6}Zr_{0.4}O₂ prepared by the novel technology exhibited good dispersion and reducibility, which resulted in a high catalytic activity of the corresponding CuO/Ce_{0.6}Zr_{0.4}O₂ catalyst for CO oxidation^[24].

In this paper, the Ce_{0.6}Zr_{0.4}O₂ mixed oxide, which was synthesized by a microwave-assisted heating and refluxing process^[23], was used as a support for the preparation of a series of CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts with different CuO contents. The prepared catalysts were characterized by means of N₂ adsorption, XRD, TEM, Raman, TPR and their catalytic activities for CO oxidation were evaluated by a microreactor-GC system. The influence of the CuO content on their catalytic behaviors for CO oxidation was investigated and correlated to their physico-chemical properties.

1 Experimental

1.1 Preparation of samples

Ce_{0.6}Zr_{0.4}O₂ mixed oxide, which was used as a carrier

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* **Corresponding author:** MAO Dongsen (E-mail: dsmao@sit.edu.cn; Tel.: +86-21-60873625)

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to prepare the supported-CuO catalyst, was prepared by the co-precipitation method combined with microwave-assisted heating reflux according to the procedure presented in the Ref. [23]. The CuO/Ce_{0.6}Zr_{0.4}O₂ catalyst was prepared by the conventional incipient-wetness impregnation method. The experiments were carried out as follows: desired amount of Cu(NO₃)₂·3H₂O was dissolved in appropriate amount of deionized water, and then the Ce_{0.6}Zr_{0.4}O₂ sample was slowly added into the solution with ample stirring. After having been impregnated quiescently at room temperature for 4 h, the prepared sample was dried at 90 °C overnight, and then calcined in a muffle furnace for 4 h at 500 °C in air. The prepared catalyst was denoted as CuO_x/CZ (*x*=1, 5, 10, 15), where the *x* represents the weight percent of CuO loading.

1.2 Sample characterization

XRD data were collected on a Philips X'Pert PRO powder diffractometer operating at 40 kV/40 mA using Cu K α radiation. The intensity data were obtained in the 2 θ range of 20°–90° with a scan rate of 0.1°/s. The lattice parameters were calculated based on Bragg's law, and the crystal size was determined by the Scherrer equation based on the (111) plane of CeO₂.

The BET surface area and BJH pore-distribution measurements were conducted by N₂ adsorption-desorption in a Micromeritics ASAP-2020 instrument. Before analysis, samples were evacuated for 4 h at 250 °C in the degassing port of the instrument. The TEM images were obtained on a JEM-2100 (JEOL) instrument equipped with a slow-scan CCD camera and at an accelerating voltage of 200 kV. Samples were sonically dispersed in ethanol and deposited on a carbon coated copper grid before examination. Raman spectra were obtained by a Renishaw Invia+Reflex confocal microscope. The exciting wavelength was 514 nm with a power of *ca.* 20 mW on the sample. The resolution was ± 1 cm⁻¹. The scanning range was 200–1200 cm⁻¹ in air.

The reduction properties of catalysts were measured by means of the temperature-programmed reduction of H₂ (H₂-TPR). A 50 mg sample was placed in the middle of the quartz tube, into which the mixed flow (50 mL/min) of 10% H₂ in N₂ was introduced. The temperature of the sample was programmed to rise at a constant rate of 10 °C/min and the amount of H₂ uptake during the reduction was measured by a thermal conductivity detector (TCD). The water produced in TPR process was trapped in a 0.5 nm molecular sieve.

1.3 Catalytic activity test

The catalytic activity measurement for CO oxidation was carried out in a fixed bed reactor (6 mm i.d.) under atmospheric pressure. 0.2 g of prepared catalyst powders of 40–60 mesh size were diluted with 0.6 g quartz sand

and placed in the middle of the reactor tube. Temperature was measured directly at the catalyst bed, using a thermocouple placed in the hollow shaft of the reactor. Before measurement, the sample was purged with N₂ at 200 °C for 30 min to remove the impurities and then cooled to ambient temperature. After that, the mixed gases (1 vol.% CO and 1 vol.% O₂ in N₂) were switched on with a flow rate of 45 mL/min. The reactant and product compositions were analyzed on-line by a GC9790A gas chromatograph equipped with a TCD (Wenling Fuli plant, Zhejiang).

2 Results and discussion

2.1 N₂ adsorption and TEM characterization

The BET surface areas, pore volumes and pore sizes of the support Ce_{0.6}Zr_{0.4}O₂ and the catalysts CuO/Ce_{0.6}Zr_{0.4}O₂ were measured by N₂ adsorption-desorption and the results are shown in Table 1.

From Table 1, we can see that the surface areas, pore volumes and pore sizes of the CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts are all smaller than those of support Ce_{0.6}Zr_{0.4}O₂, and decreased monotonously when the CuO loading increased from 1% to 15%, which is mainly caused by the fact that the CuO particles dispersed on the surface of the catalyst and blocked part of the pores.

Fig. 1 (a) and (b) show N₂ desorption-adsorption isotherms and BJH pore size distribution of the support and catalysts, respectively. According to classification of gas adsorption isotherm by IUPAC^[25], the shape of the isotherms are almost the same (type IV) with H₂-type hysteresis loop in Fig. 1(a). In the low-pressure range of $p/p_0 \leq 0.6$, the adsorption branch of the five samples slowly ascended; while in the high-pressure range of $p/p_0 > 0.6$, the adsorption branch steeply ascended. The results showed that all the samples possessed dense mesopores^[26]. In the low-pressure range, the micropores in the samples played a dominant role in the adsorptive capacity. The adsorptive capacity of support Ce_{0.6}Zr_{0.4}O₂ was larger than that of catalyst CuO/Ce_{0.6}Zr_{0.4}O₂. It was indicated that a part of the micropores in catalyst CuO/Ce_{0.6}Zr_{0.4}O₂ was stuffed by fine CuO particles. In high-pressure range, the mesopores in the samples drew decisive influence on the adsorptive capacity. It was indicated that the mesopores in these samples were densely

Table 1 BET surface areas and pore structure data of support and catalysts

Sample	Surface area/(m ² /g)	Pore volume/(cm ³ /g)	Pore size/nm
Ce _{0.6} Zr _{0.4} O ₂	170.8	0.408	9.6
CuO1/CZ	151.8	0.339	9.0
CuO5/CZ	140.2	0.307	8.8
CuO10/CZ	127.9	0.277	8.7
CuO15/CZ	119.1	0.256	8.6

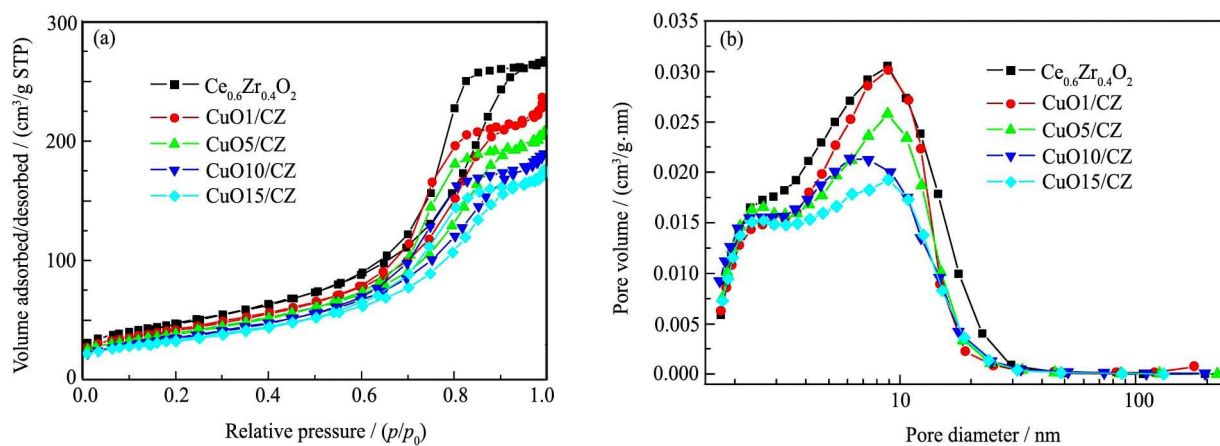


Fig. 1 Isotherm linear plots (a) and pore-size distribution (b) of the samples

distributed. However, the mesopores volume of CuO/Ce_{0.6}Zr_{0.4}O₂ catalyst obviously decreased as the CuO loading increased. Among them, the pore volume of CuO15/CZ was the lowest. From Fig. 1(b), it can be seen that after supporting CuO the average pore size of Ce_{0.6}Zr_{0.4}O₂ decreased slightly, but the pore volume decreased more evidently. Thus, we speculate that CuO particles were preferentially adsorbed in the micropores and then uniformly dispersed on the support surface, which resulted in pore size distribution remained basically unchanged, but the pore volume decreased noticeably.

The TEM images of CuO1/CZ and CuO10/CZ catalysts are shown in Fig. 2. We can see from Fig. 2(a) that most of CuO1/CZ morphology was spherical. The average crystallite size was 4–6 nm, which was in good agreement with the values obtained from XRD analysis (see Section 2.2). Furthermore, large CuO particles were not spotted in this sample. In contrast, large irregular particles corresponding to crystalline CuO particles are observed from Fig. 2(b), and the particle sizes of which were 20–35 nm, which was also in good agreement with the values obtained from XRD analysis (see Table 2).

2.2 XRD and Raman spectroscopy

XRD patterns of the Ce_{0.6}Zr_{0.4}O₂ support and CuO/

Ce_{0.6}Zr_{0.4}O₂ catalysts are shown in Fig. 3. It can be seen that the CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts had the same patterns as the Ce_{0.6}Zr_{0.4}O₂ support except for two CuO characteristic peaks at $2\theta=35.5$ and 38.7° appeared with higher CuO loadings ($\geq 10\%$). The diffraction peaks at $2\theta=29.21^\circ$, 33.56° , 48.57° and 57.81° in the XRD patterns of all samples are corresponded to the cubic, fluorite structure of CeO₂^[23]. No extra peaks associated with ZrO₂ were observed, which implied that Zr⁴⁺ had been incorporated into the CeO₂ lattice to form a ceria-zirconia solid solution while maintaining the fluorite structure^[23].

The average crystallite size and the lattice parameter values of Ce_{0.6}Zr_{0.4}O₂ support and corresponding CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts are listed in Table 2. It was noted that the particle sizes of these Ce_{0.6}Zr_{0.4}O₂ were close to each other. On the other hand, when the CuO loading was 1% and 5%, no peaks attributed to CuO crystal phase were observed for the CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts, which indicated that CuO was finely dispersed on support surface or inserted into the crystal lattice of Ce_{0.6}Zr_{0.4}O₂^[16]. However, two CuO characteristic peaks appeared noticeably when the CuO loading was increased to 10%. Furthermore, the crystal peaks became stronger and sharper when the CuO loading increased further to 15%, indicating that the particle sizes of crystalline CuO became bigger as the CuO loading in-

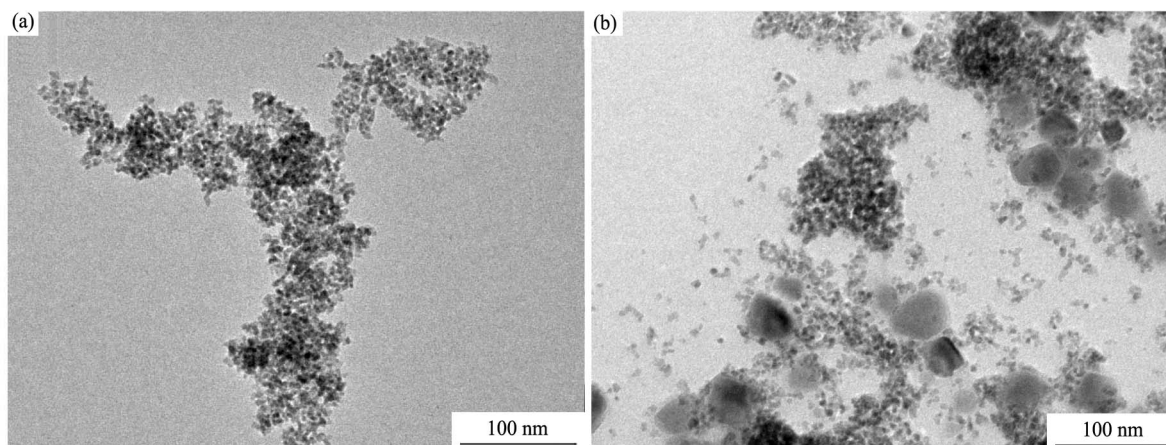


Fig. 2 TEM images of CuO1/CZ (a) and CuO10/CZ (b) samples

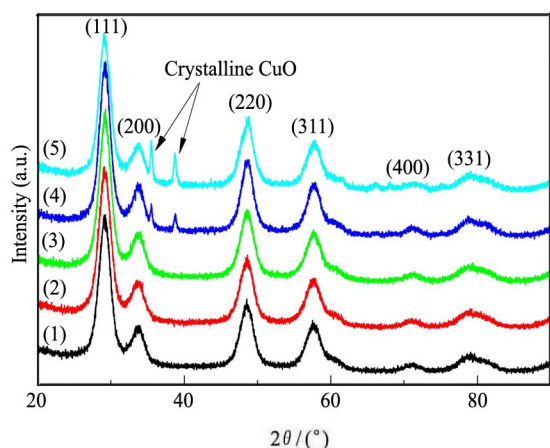


Fig. 3 XRD patterns of CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts with different CuO loadings

(1) 0%; (2) 1%; (3) 5%; (4) 10%; (5) 15%

Table 2 Crystallite size and cell parameter *a* of Ce_{0.6}Zr_{0.4}O₂ and CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts

Sample	Support crystallite size/nm	CuO crystallite size/nm	Cell parameter <i>a</i> /nm
Ce _{0.6} Zr _{0.4} O ₂	4.5	–	0.5294
CuO1/CZ	4.5	–	0.5291
CuO5/CZ	4.6	–	0.5285
CuO10/CZ	4.8	26.3	0.5279
CuO15/CZ	4.8	35.4	0.5281

creased^[10]. This was also verified by the particle sizes of crystalline CuO determined by Scherrer equation shown in Table 2.

As can be observed from Table 2, there is a decrease in the lattice parameter values of all the catalysts in comparison to that of Ce_{0.6}Zr_{0.4}O₂ support. This results from the fact that the ionic radius of Cu²⁺ (0.079 nm) is smaller than that of Ce⁴⁺ (0.097 nm) and Zr⁴⁺ (0.084 nm). A little amount of Cu²⁺ replaced the position of Ce⁴⁺ or Zr⁴⁺ in CeO₂-ZrO₂ solid solution and caused shrinkage of the lattice in the preparation process of the catalysts. And the cell parameter *a* would gradually decrease with an increase of CuO loading^[7].

Lattice parameter estimations provide useful information for seeking out the existence of Cu²⁺ in the ceria-zirconia lattice. However, the XRD technique does not provide accurate identification of oxygen defects in the structure as a result of foreign cations, while Raman spectroscopy may resolve the problem. As shown in Fig. 4, all the CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts showed prominent broad peaks at ~466 and ~615 cm⁻¹ and a weak band at ~295 cm⁻¹. Among them, the band at ~466 cm⁻¹ was ascribed to the Raman active *F*_{2g} mode of CeO₂; and the bands at ~615 and ~295 cm⁻¹ could be linked to lattice defects, which resulted from the formation of oxygen vacancies^[7,16]. According to Ref. [7], the ratio of the peak area at ~615 and ~466 cm⁻¹ (i.e. *A*₆₁₅/*A*₄₆₆) can be used to indicate the concentration of oxygen vacancies,

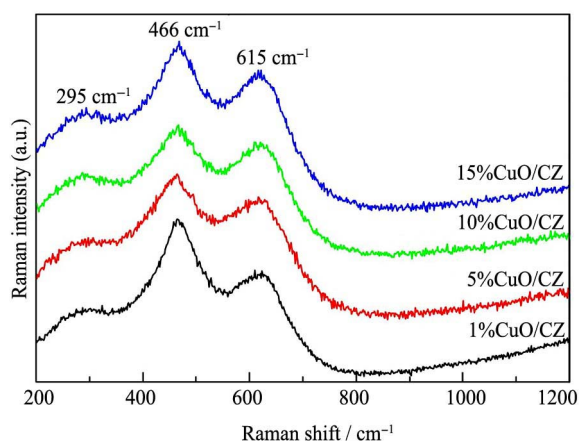


Fig. 4 Raman spectra of CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts with different CuO loadings

and thus, we can assess the influence of the CuO loading on the oxygen vacancies concentration. The calculation results (Table 3) showed that the *A*₆₁₅/*A*₄₆₆ values of CuO_{*x*}/CZ (*x*=1, 5, 10, 15) catalysts were 14%, 37%, 41% and 38%, respectively. This result indicated that among all the CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts, the oxygen vacancies concentration in CuO10/CZ catalyst was the highest (see Table 3).

2.3 Temperature-programmed reduction of the catalysts

Fig. 5 shows the TPR profiles of CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts with various CuO loadings and pure crystalline

Table 3 Oxygen vacancies concentration, reduction peak temperature and ‘light-off’ temperature of CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts with various CuO loadings

Catalyst	Reduction peak temperature/°C			<i>A</i> ₆₁₅ / <i>A</i> ₄₆₆	<i>T</i> ₁₀₀ /°C
	α peak	β peak	γ peak		
CuO1/CZ	221	254	–	14	145
CuO5/CZ	178	208	–	37	100
CuO10/CZ	161	199	223	41	95
CuO15/CZ	169	207	231	38	98

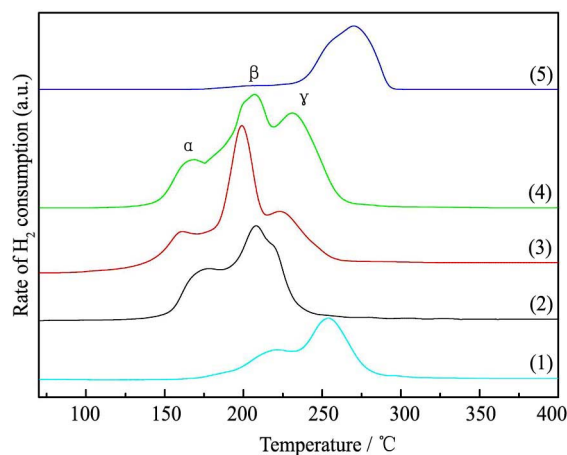


Fig. 5 H₂-TPR profiles of CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts with different CuO loadings and crystalline CuO

(1) 1%; (2) 5%; (3) 10%; (4) 15%; (5) Crystalline CuO

CuO. As seen in Fig. 5, only one peak γ appeared at 270 °C in pure CuO sample. The results show that the reduction temperature of the CuO/CZ catalysts was much lower than that in pure CuO, implying the existence of synergistic interaction between CuO and CZ support and thus the promotion of reduction of CuO by CZ^[9,27]. On the other hand, two reduction peaks, denoted as α and β , respectively, were observed in TPR profile of the CuO1/CZ catalyst. When the CuO content was increased to 5%, the reduction temperatures of both α and β peaks shifted to lower values. A similar phenomenon was also reported by Wang et al.^[27] over the CuO-ZrO₂-CeO₂ mixed oxide prepared by citrate method. This shift in reduction temperature is not totally clear, but as Aguila et al.^[28] suggested, one can postulate that at low Cu/support ratio, Cu existed as isolated Cu²⁺ species, which strongly interact with the support. When increasing the Cu content, it occupies highly dispersed surface sites but with a weaker interaction with the support, which promotes the reduction of copper. When the CuO content was increased further to 10% and 15%, a third reduction peak γ besides α and β was observed, which can be assigned to the reduction of bulk CuO. Furthermore, when the CuO loading increased from 10% to 15%, the intensity of γ peak increased significantly, suggesting the formation of more bulk CuO. This result was in good line with that obtained by XRD analysis.

The temperatures of the reduction peaks in the profiles for these CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts are shown in Table 3. According to the reduction peak temperature, the reducibility of these CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts increased in the order of CuO1/CZ < CuO5/CZ < CuO15/CZ < CuO10/CZ. Especially, the CuO10/CZ catalyst possesses the best reducibility among these catalysts.

2.4 Performance of the catalysts in CO oxidation

Fig. 6 shows the catalytic activities in CO oxidation of CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts with various CuO loadings. The results present a similar behavior that the CO conversion of all the CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts increased

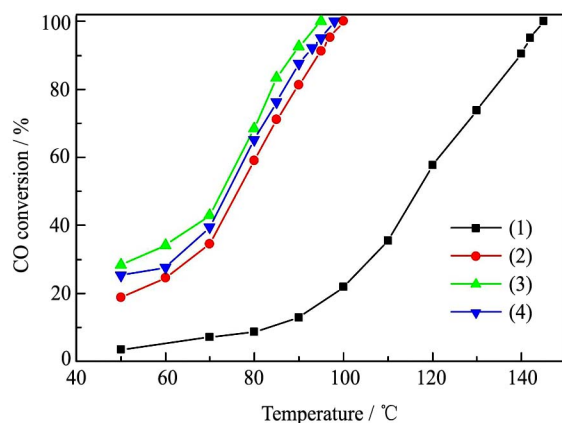


Fig. 6 Catalytic activity for CO oxidation of different CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts with various CuO loadings (1) 1%; (2) 5%; (3) 10%; (4) 15%

with the increase in the reaction temperature. The “light-off” temperatures for 100% CO conversion of the catalysts are presented in Table 3. As reported previously, the activity of pure Ce_{0.6}Zr_{0.4}O₂ for CO oxidation was very low, its T_{100} being as high as 340 °C under the present reaction conditions^[23]. Clearly, the addition of CuO enhances the CO oxidation activity of Ce_{0.6}Zr_{0.4}O₂ greatly. Moreover, it can be observed that the activity sequence of the prepared catalysts is: CuO1/CZ << CuO5/CZ < CuO15/CZ < CuO10/CZ. That is to say, the catalytic activity of CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts rose with the CuO loading increasing, but started to decrease when the CuO loading exceeds 10%. It was indicated that increasing the CuO loading could not always promote the catalytic activity, and the 10% CuO/Ce_{0.6}Zr_{0.4}O₂ catalyst exhibited the highest catalytic activity.

The effect of CuO content on catalytic activity of CuO/CeO₂-ZrO₂ was investigated by many other researchers and different conclusions were obtained. For example, Wang^[4,5], Cao^[9,10] and Chen and Zhu^[3,12] research groups found that the CO conversion increased first with CuO content increasing, passing through a maximum, then decreased at higher CuO contents. That is to say, the excess CuO would deteriorate the catalytic activity. On the other hand, Zhong et al.^[29] and Wang et al.^[27] reported that the CO oxidation activity increased with Cu-loading when it was in the range of the dispersion threshold and stabilized after it exceeded the dispersion threshold. In other words, when the Cu loading increased further, the activity of catalyst hardly changed. Obviously, our result is consistent with the former conclusion^[3-5,9-12].

There are many factors that affect the activity of the CuO/CeO₂-ZrO₂ catalyst for CO oxidation, mainly relating to the close interaction between Cu species and CeO₂^[1,11]. It has been well demonstrated that the highly dispersed and fine CuO particles which interact with CeO₂ are mainly responsible for the high activity of the catalyst for CO oxidation^[3-5,9-12]. As shown by the H₂-TPR results, the amount of the highly dispersed and fine CuO particles which interact with CeO₂ increased when the CuO content increased from 1% to 10%, which accounts for the increase in activity of the catalyst. However, when the CuO content was further increased to 15%, the amount of the highly dispersed and fine CuO particles which interact with CeO₂ decreased, while the amount of bulk CuO increased significantly. It is generally accepted that the bulk CuO not only cannot contribute to the high activity but also deteriorate the activity since they could cover some of the active sites^[9,10]. Accordingly, the activity of CuO15/CZ was lower than that of CuO10/CZ.

On the other hand, combining the activity test result with that of Raman study we can find that the order of activity of different CuO/Ce_{0.6}Zr_{0.4}O₂ catalysts was the

same as that of the concentration of the surface oxygen vacancy on the catalysts. This result suggested that the activity of $\text{CuO/Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts for CO oxidation was closely related to the concentration of the surface oxygen vacancy, which is consistent with that reported by Hong and co-workers^[7].

To evaluate the stability of the catalytic activity, a long-term test on the most efficient CuO10/CZ catalyst was carried out at 95 °C. The result (not shown here) showed that the CO conversion maintained at about 100% and no obvious deactivation was observed for up to 48 h, indicating that the CuO10/CZ catalyst exhibited a stable catalytic performance for CO oxidation.

3 Conclusions

A series of $\text{CuO/Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts with different CuO contents were prepared by impregnation method to investigate the effect of CuO content on the catalytic performance for CO oxidation. The result indicated that the catalytic activity of the $\text{CuO/Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst for CO oxidation was greatly influenced by the CuO content. With the CuO content increasing, the CO conversion increased first, passing through a maximum, and then decreased at higher CuO contents. The catalyst with 10 wt.% CuO exhibited the best catalytic activity in CO oxidation, which was due to the high dispersion and reducibility of CuO, and high oxygen vacancy concentration in the catalyst.

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