

Role of Cu-O-Ce Interface on Low-Temperature CO Oxidation over CuO/CeO₂

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Abstract

Cu/CeO₂ exhibits high CO oxidation activity comparable to noble metal catalysts below 100 °C. To clarify the interaction between CuO and CeO₂, the effect of Cu content on CO oxidation activity of Cu/CeO₂ was investigated in the low Cu content region (0.05–2 wt%). The CO oxidation activity per catalyst weight increased significantly with increasing Cu content up to 0.5 wt%, while the increase slowed down at higher Cu content. Turnover frequency (CO oxidation activity per supported Cu) became maximized at 0.5 wt% and then decreased with further increase in Cu content. XRD and XAFS analyses revealed that the supported Cu was well dispersed as divalent Cu oxide. STEM images revealed that the particle size of CuO was approximately 1.0–1.4 nm. When pulse CO oxidation was performed at 60 °C in the absence of oxygen, the produced CO₂ was comparable to 37% oxygen in CuO, which corresponds to the periphery of CuO islands assuming a CuO monolayer. The results suggested that the Cu-O-Ce bond at the periphery of CuO is the active species.

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1 Introduction

CO oxidation is a typical reaction of heterogeneous catalysis and is applied for various practical applications, such as one of the roles of automotive three-way catalysts [1-4], preferential oxidation of CO in excess hydrogen (PROX) [5-7], and so on. Typically, supported noble metal catalysts such as Pt/Al₂O₃ are often used as catalysts [3,5,7-9]. Alternatively, Au nanoparticles are attracting much attention for their CO oxidation activity even at low temperatures around 0°C [10]. On the other hand, due to the scarcity, high cost, and unstable supply of resources, there is a need for the development of CO oxidation catalysts using non-noble metals. As active species of non-noble metals, Co₃O₄, MnO₂, and NiO, which have p-type semiconducting properties, hold potential catalytic capability for the oxidation of CO. [11] Furthermore, transition metal oxides such as metal oxides of Ce, Mn, Cu, Ni, Co, and Fe have been reported as active species and supports for the catalytic CO oxidation [12-16]. Especially, CeO₂ has attracted much attention due to its excellent oxygen storage capacity (OSC), Ce³⁺/Ce⁴⁺ redox electron pair, and abundant oxygen vacancies [17-20]. Among these, high CO oxidation activity of Cu/CeO₂ catalysts has been reported [6,7, 21-31]. Avgouropoulos et al. reported that CuO-CeO₂ catalysts exhibited high CO oxidation activity in excess hydrogen comparable to Pt/ γ -Al₂O₃ and Au/ α -Fe₂O₃ [6, 7]. Liu et al. found that the dispersed Cu clusters on CeO₂ provide highly active sites for CO oxidation by forming Cu¹⁺ species for CO chemisorption [22]. Furthermore, the

importance of the interface between CeO₂ and CuO is emphasized, which leads to the formation of abundant oxygen vacancies as active sites for catalytic oxidation [22]. Gamarra et al. clarified that CO is oxidized at interfacial positions of the dispersed copper oxide entities through comparison of Cu/CeO₂ supported catalyst and Cu_{0.2}Ce_{0.8}O₂ mixed oxide catalyst [23].

Despite numerous reports on Cu/CeO₂ catalysts, the range of Cu content reported to date has been limited to approximately 2 wt% to 15 wt%, and the lower Cu content region is not sufficiently investigated. This is probably because the highest CO oxidation activity per unit weight can be obtained above 2wt%. However, essentially, the metal-support interaction becomes stronger in the low Cu content region, and unique effects should appear more clearly. In this study, we investigated the CO oxidation reaction on a Cu/CeO₂ catalyst in the low Cu content region (0.05–2 wt%). Maximum activity per unit of Cu was observed at 0.5 wt%. The origin of the high activity was suggested to be the periphery of Cu nanoparticles, i.e., the interface of Cu nanoparticles and CeO₂ support.

2 Experimental

Catalyst Preparation: Metal-supported CeO₂ catalysts were prepared by a conventional impregnation method. CeO₂ (JRC-CEO-3, 81.4 m² g⁻¹, supplied from the Committee of Japan Reference Catalyst) was dispersed in distilled water (50 mL) and stirred with metal nitrate (Cu, Ru, Pt, Co, and Ni) solution for 1 h at room temperature. After stirring, the slurry was concentrated in a rotary evaporator at 80 °C, and the solid was collected and dried overnight in an oven at the same temperature. The dried precursor was calcined in air at 400 °C. The metal content was 0.5 wt% for the screening study, and 0.05 to 2 wt% for the Cu/CeO₂ study.

XRD (X-Ray Diffraction): The structure of the catalysts was evaluated using a laboratory-scale XRD (Rigaku MiniFlex diffractometer with Cu K α radiation at 45 kV and 10 mA).

HAADF-STEM (High-Angle Annular Dark Field Scanning Transmission Electron Microscopy): Catalysts were sonicated in 3 mL of water for 30 min. The supernatant was drop-cast onto Cu TEM grids and dried under vacuum for 12 h. TEM images were acquired on a JEM-ARM200F operating at 200 kV and analyzed with Gatan Microscopy Suite v3.43 (AMETEK).

XANES and EXAFS (X-ray Absorption Near-Edge Structure and Extended X-ray Absorption Fine Structure): Prior to the measurement, the samples were pretreated in a flow of 10%O₂/N₂ at 300 °C for 15 min, which corresponded to the pretreatment protocol employed in the preceding catalytic activity testing procedure. Catalysts (50 mg) were pressed into 10 mm disks. Cu K-edge XAFS spectra were recorded at the Aichi Synchrotron Radiation Center (BL11S2) with an Si (111) monochromator; Cu foil was measured concurrently for energy calibration. XANES normalization and EXAFS Fourier transforms were carried out using Athena 2 software. Fourier transform extended X-ray absorption fine structure (FT-EXAFS) spectra were obtained by Fourier transform of the k^2 -weighted $\chi(k)$ function over the range $3 < k < 13 \text{ \AA}^{-1}$.

Nitrogen adsorption isotherms: Nitrogen adsorption–desorption isotherms were recorded at –196 °C (77 K) on a BELSORP-mini II (MicrotracBEL). Before analysis, ca. 200 mg of sample was

outgassed under high vacuum ($< 3 \times 10^{-3}$ Pa) at 350 °C for 3 h to eliminate physisorbed moisture. Specific surface areas were evaluated from the adsorption isotherms by applying the Brunauer–Emmett–Teller (BET) model over the relative pressure window $P/P_0 = 0.05–0.30$.

Activity Tests. Catalytic performance in CO oxidation was evaluated in a flow reactor. In a Pyrex U-shaped tube with 6 mm outer diameter and 4 mm inner diameter, 25 mg of catalyst was fixed with glass wool and pretreated in a flow of 10%O₂/N₂ at 300 °C for 15 min. The flow rate was 100 mL/min (SV=240,000 mL g_{cat}⁻¹h⁻¹). After cooling to 50 °C, the flow gas was switched to a mixture of 0.3%CO, 10%O₂, and N₂ as a balance, and the catalyst temperature was increased from 50 °C to 300 °C stepwise in increments of 50°C. The effluent gas was analyzed using a CO/CO₂ analyzer (Shimadzu CGT-7100), and the steady-state activities were determined. The quality of the materials was as follows: carbon monoxide (CO, >99.5%, Sogo-Kariya sanso), oxygen (O₂, 99.99%, Sogo-Kariya sanso), and nitrogen (N₂, 99.99%, Sogo-Kariya sanso). CO conversion and turnover frequency (TOF) were defined as the following equations:

$$\text{CO conversion(\%)} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}}$$

$$\text{TOF}(h^{-1}) = \frac{\text{Reaction rate (mol g}_{\text{catal}}^{-1}h^{-1})}{\text{Loaded metal (mol g}_{\text{catal}}^{-1})}$$

Anaerobic CO oxidation was carried out using the same apparatus at a flow rate of 100 mL min⁻¹. A 25 mg catalyst was pretreated at 300 °C for 15 min in a flow of 10%O₂/N₂, cooled down to 60 °C in a flow of 10%O₂/N₂, purged in pure Ar at 60 °C, and finally a flow gas was switched to 0.3% CO/Ar at 60 °C.

3 Results and Discussion

3.1 CO oxidation

First, the CO oxidation activity of 0.5 wt% Ru, Cu, Pt, Co, and Ni supported CeO₂ catalysts was screened. Fig. S1 shows XRD patterns of the prepared catalysts. The series of CeO₂-supported catalysts only showed the diffraction lines attributed to CeO₂ (JCPDS Card # 34-0394), suggesting that Cu species are highly dispersed on the CeO₂ surface. Fig. S2 shows light-off curves of CO oxidation. Below 150 °C, Ru/CeO₂ and Cu/CeO₂ showed higher activity than Pt/CeO₂. Especially, it should be noted that the non-noble metal Cu/CeO₂ showed higher activity than Pt/CeO₂, and far higher activity than other non-noble metal catalysts (Co/CeO₂ and Ni/CeO₂). Afterward, the source of CeO₂ support and calcination temperature were optimized using 0.5wt% Cu/CeO₂. Calcination temperature at 400 °C gave the best activity. (Fig. S3)

The effect of Cu content in Cu/CeO₂ catalysts was evaluated using a series of Cu/CeO₂ having Cu content of 0.05, 0.1, 0.3, 0.5, 1, and 2 wt%. Fig. 1 shows the CO conversion as a function of reaction temperature. As increase in the Cu content from 0.05 to 1 wt%, the CO conversion increased. The light-off temperature was 60 °C for 0.1 and 0.3 wt% Cu/CeO₂, while it was 40-50 °C for 0.5, 1, and

2 wt% Cu/CeO₂. Interestingly, CO conversions of 0.5 wt% Cu/CeO₂ and 1 wt% Cu/CeO₂ are almost the same below 60 °C, while 1 wt% Cu/CeO₂ showed higher activity at higher temperatures. As Cu content increased from 1 to 2 wt%, the CO oxidation activity decreased. The CO oxidation activity of pure CeO₂ was negligible below 100 °C. To evaluate the intrinsic activity of supported Cu species, the reaction rate at 60 °C was evaluated at a low conversion level (10-30 %), and turnover frequencies (TOF) of each catalyst were compared. This is because CO oxidation activity at lower temperatures attracted much attention [32]. The blue squares in Fig. 2 illustrate the reaction rate per catalyst weight (mol g_{catal}⁻¹ h⁻¹) at 60 °C, which increased steeply from 0 to 0.5 wt% and gradually from 0.5 to 2 wt%. The red circles in Fig. 2 show turnover frequency (TOF), which is the reaction rate per supported Cu atom (h⁻¹). The TOF became maximum at 0.5 wt%, and further addition of Cu decreased TOF. The TOF at 60 °C was around 5 times higher than that of Cu/CeO₂ catalysts without further modification in the literature (Fig. S4 and Table S1) [24-31]. Probably, this is because of the lower Cu content (below 1 wt%) of our catalyst. The lower content of Cu may result in closer interaction of Cu species with the CeO₂ support. However, the TOF of our catalyst was around 1/3 of hydrogen pretreated Cu/CeO₂ reported by Tian et al. [33] (Table S2). To examine the reason for such high efficiency of Cu species, the detailed structure of supported Cu species of Cu/CeO₂ is examined in the next section.

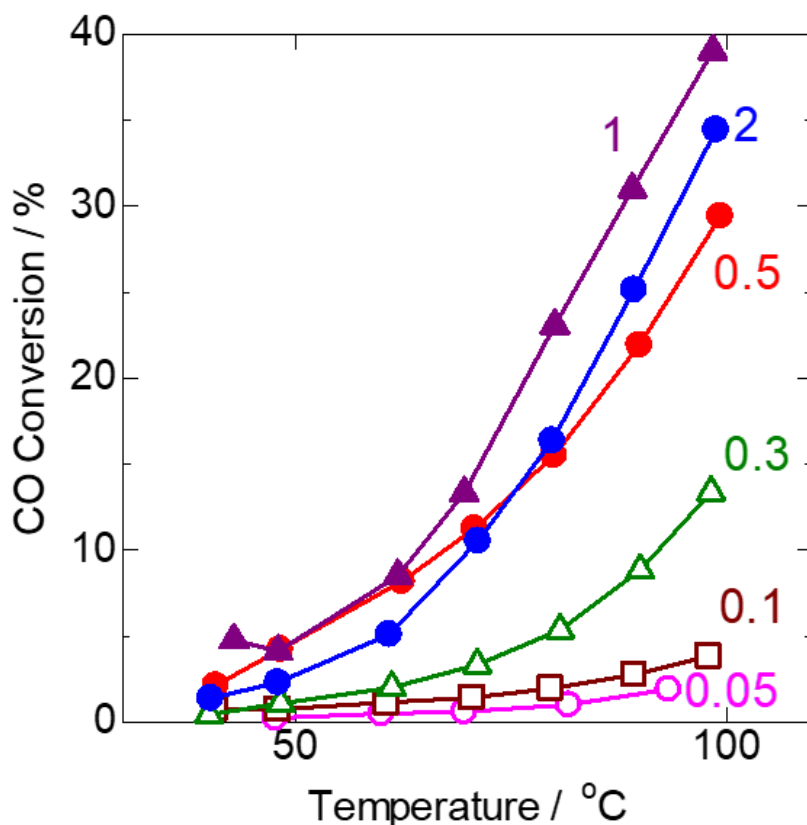


Fig. 1 CO conversion on Cu/CeO₂ catalysts having Cu content from 0.05 to 2 wt% as a function of reaction temperature. The numbers indicate the Cu content. Reaction conditions: 0.3%CO, 10%O₂, N₂ balance, catalyst 25 mg, total flow rate 100 mL/min.

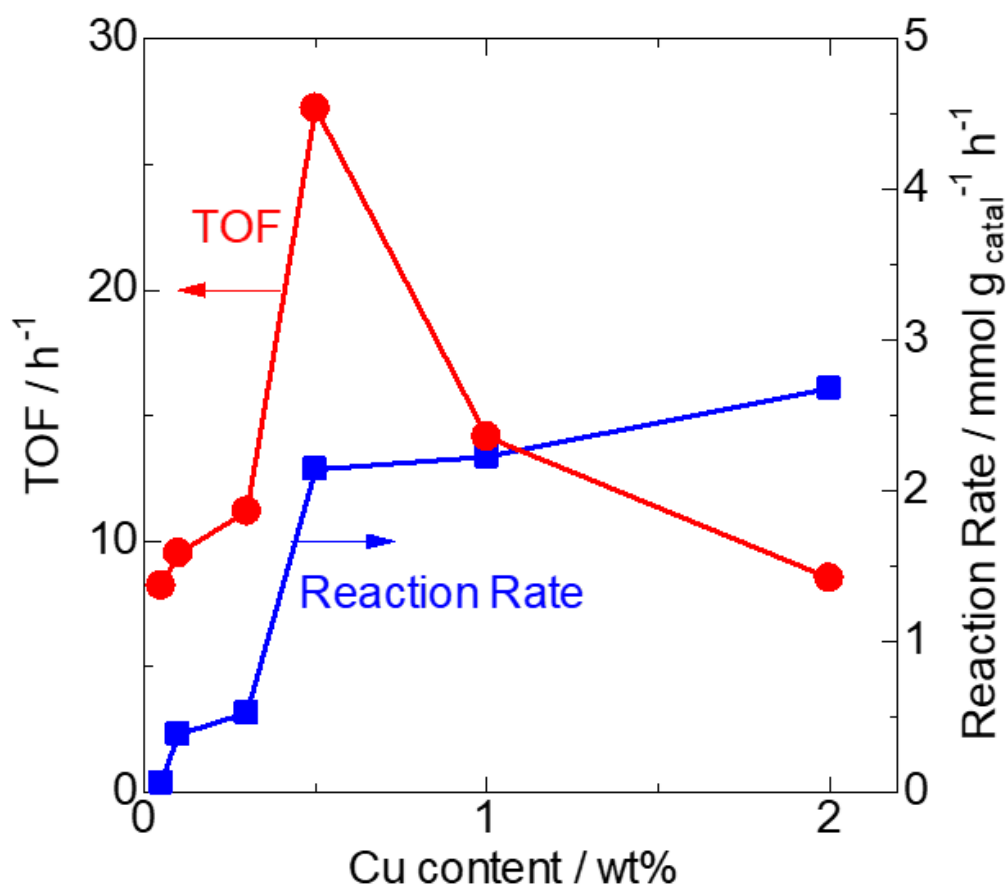


Fig. 2 Reaction rate of CO at 60 °C and turnover frequency (TOF, Reaction rate/supported Cu, h⁻¹) as a function of Cu content.

3.2 Characterizations

Fig. 3 shows the XRD patterns of the series of Cu/CeO₂ catalysts having Cu content from 0.05 to 2 wt%. For all the catalysts, the patterns assignable to CeO₂ (JCPDS card #34-0394) are observed. Diffraction lines attributable to Cu, CuO, or Cu₂O were not observed. The diffraction lines of CeO₂ were not significantly shifted. The results indicate that the loaded Cu is highly dispersed on the CeO₂ surface.

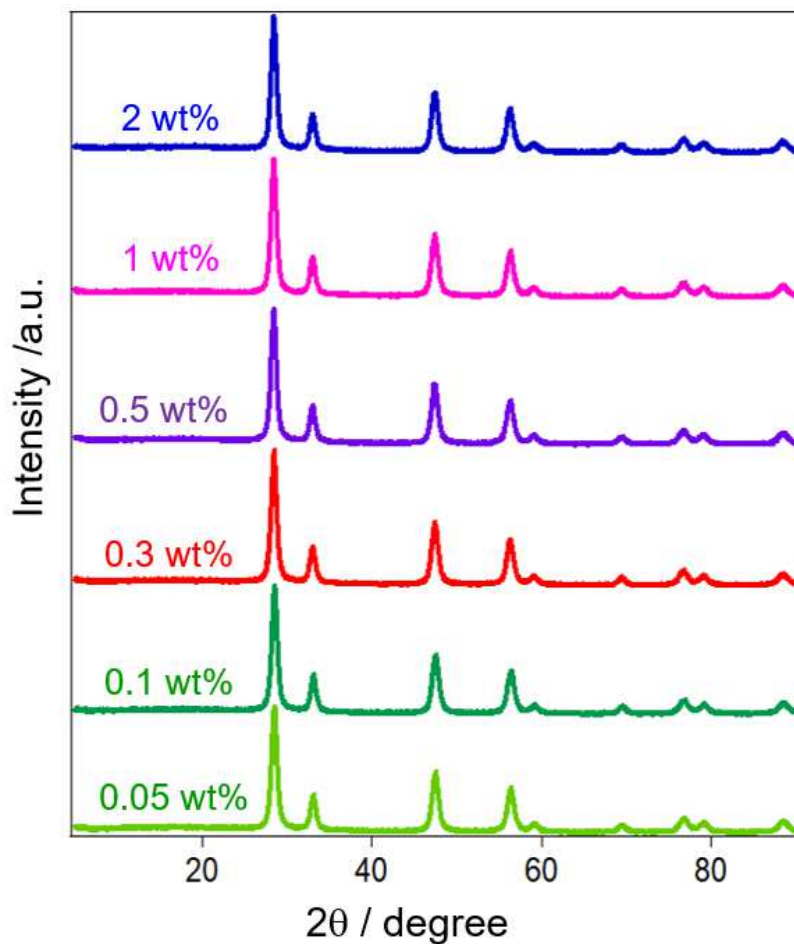


Fig. 3 XRD patterns of the series of Cu/CeO₂ catalysts having Cu content from 0.05 to 2 wt%.

Fig. 4 shows the Cu K-edge XANES spectra of Cu/CeO₂ catalysts and the reference samples. The XANES spectrum of Cu foil exhibits the edge absorption at 8979 eV together with a well-resolved doublet in the post-edge region. As increase in the oxidation state of Cu, Cu₂O, Cu(NO₃)₂, and CuO, the edge absorption shifted to higher energy and the white-line intensity became stronger. The edge shift towards higher energies with increasing valence of Cu has also been reported in the literature [34-37]. The white-line of Cu/CeO₂ catalysts is at 8996 eV, which is the same as Cu(NO₃)₂ and CuO, suggesting that oxidized Cu is supported on CeO₂ in a divalent state. In the spectra of Cu/CeO₂ catalysts, the pre-edge observed at 8984 eV in CuO is not clearly observed. It is reported that the near-edge transition $1s \rightarrow 3d$ is sensitive to the presence or absence of a symmetry center, and its intensity increases with increasing distortion from the center of tetragonal symmetry in relation to an increase in p - d orbital mixing [37]. Therefore, the XANES spectra suggest that the Cu species supported on CeO₂ are basically similar to CuO, having a modified coordination state around Cu.

The EXAFS measurements in the Cu K-edge region were performed to analyze the local structure of Cu species. The $k^3w(k)$ oscillations were Fourier transformed as shown in Fig. 5. As for Cu foil, a strong peak due to Cu-Cu was observed. The other reference samples exhibit two strong peaks, one around 1.48-1.64 Å due to Cu-O and the other at 2.60-2.83 Å due to Cu-Cu scattering, respectively.

In the case of Cu/CeO₂ catalysts, all the samples showed a peak due to Cu–O at 1.54 Å. A small peak due to Cu–Cu scattering was observed only in 2wt% Cu/CeO₂ at 2.54 Å. The presence of the Cu–O bond agrees well with the XANES spectra, which indicate Cu is oxidized in the divalent state. The absence of the peak of Cu–O–Cu below 1wt% indicates that the supported Cu is well dispersed or an amorphous oxide phase.

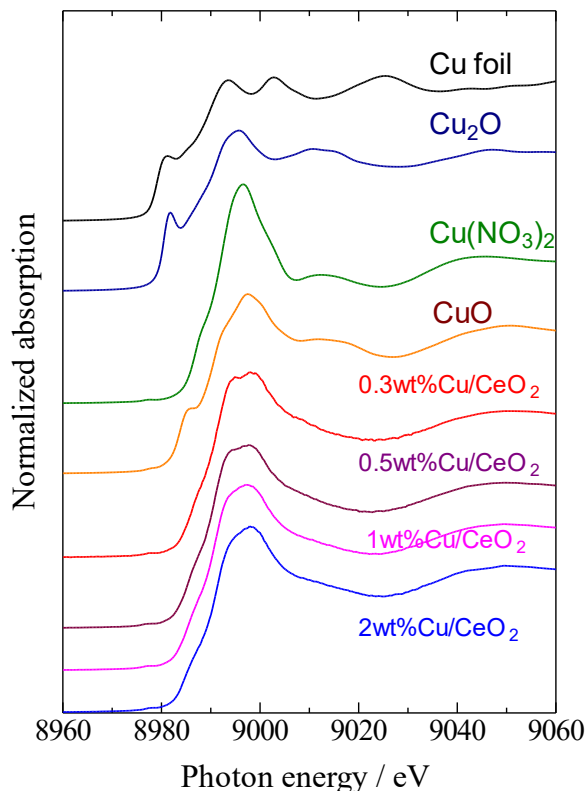


Fig. 4 Cu K-edge XANES spectra of the series of Cu/CeO₂ catalysts and reference materials (Cu foil, CuO, Cu₂O, and Cu(NO₃)₂).

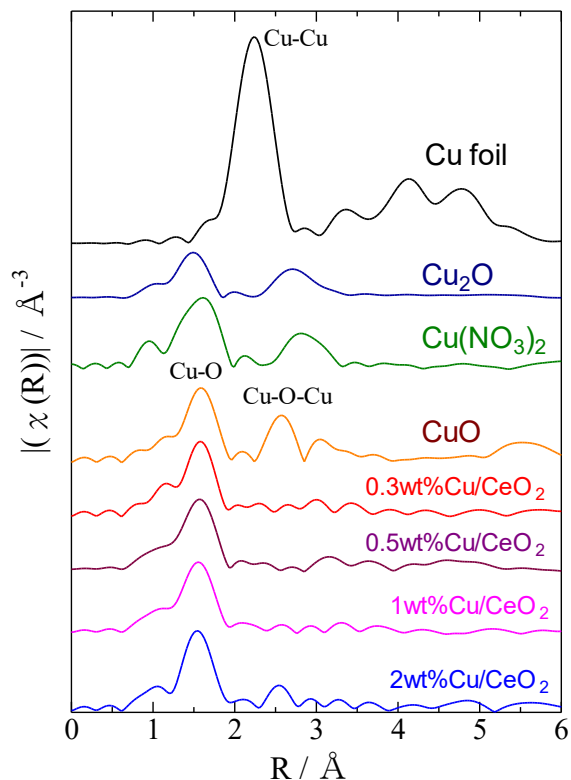


Fig. 5 Cu K-edge FT-EXAFS spectra of the series of Cu/CeO₂ catalysts and reference materials (Cu foil, CuO, Cu₂O, and Cu(NO₃)₂).

Fig. 6 shows the HAADF-STEM images of 0.5 wt% Cu/CeO₂ and 2 wt% Cu/CeO₂. Due to the difference in atomic weight, CeO₂ can be seen as the white lattice and Cu species as the black spots. The particle size of Cu oxide can be estimated to be around 1.00 nm for 0.5 wt% Cu/CeO₂ and around 1.44 nm for 2 wt% Cu/CeO₂ (Fig. S5). The distributions of particle size of Cu species are shown in Fig. S5. From the size of Cu oxide, the coverage of Cu oxide on 0.5 wt% Cu/CeO₂ was estimated. Taking the most stable facet of (111) of CuO into account, the theoretical surface of a CuO monolayer would be 3.98 m², which is 2.5 % coverage of CeO₂ (161.3 m² g⁻¹). In the STEM image of Fig. 6 (left), CuO was observed at a sufficient size and did not appear to be aggregated, suggesting that CuO is well spread out as nearly monolayer nano-islands on CeO₂.

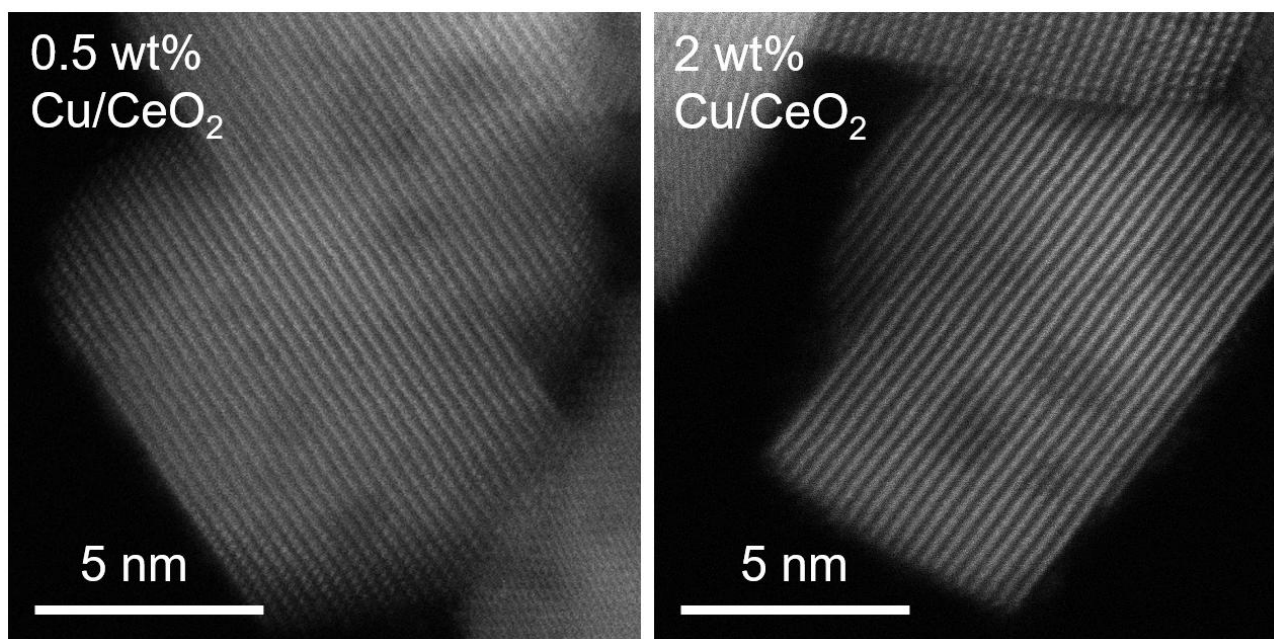


Fig. 6 shows HAADF-STEM images of (left) 0.5wt%Cu/CeO₂ and (right) 2wt%Cu/CeO₂.

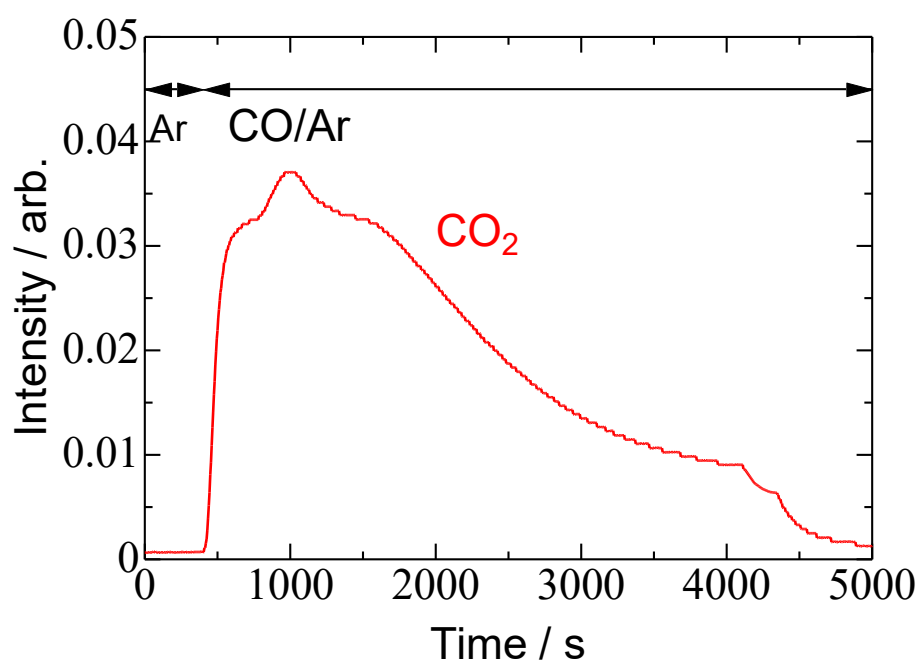
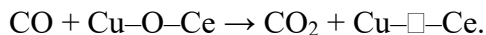


Fig. 7 Profile of profile of produced CO₂ from 0.5wt% Cu/CeO₂ in a flow of 0.3% CO/Ar at 60 °C

To determine the active species of Cu/CeO₂ for CO oxidation, anaerobic CO oxidation was carried out using 0.5wt% Cu/CeO₂. Fig. 7 shows a profile of produced CO₂ in a flow of 0.3% CO/Ar at 60 °C. The catalyst was first oxidized at 300 °C for 15 min in a flow of 10%O₂/N₂, cooled down to 60 °C, purged in Ar, and finally the flow gas was switched to 0.3% CO/Ar at 60 °C. The total amount of produced CO₂ was 0.73 μmol g⁻¹. Compared with the total amount of supported Cu of 1.97 μmol g⁻¹,

37% of oxygen contributed to the anaerobic CO oxidation. Assuming a circular island of CuO having a 1.0 nm diameter, using a Cu–O bond of 0.194 nm [38], the peripheral oxygen should be 35% of the total CuO monolayer island (Fig. S6). The ratio of peripheral oxygen agrees well with that of the produced CO₂ during anaerobic CO oxidation. This estimation suggests that the lattice oxygen in the Cu–O–Ce bond located at the CuO periphery contributes to the CO oxidation in the following equation:



These results are consistent with previous reports that activity improves when CuO and CeO₂ are well mixed. Gamarra et al. reported that the higher CO oxidation activity was obtained on a CuO–CeO₂ mixed oxide catalyst than on a Cu/CeO₂ supported catalyst [23]. Jia et al. reported that CuO(5)/CeO₂ and CeO₂(5)/CuO calcined at 500°C show the same CO oxidation activity [39]. Wang et al. investigated the effect of calcination temperature of the Cu–CeO₂ catalyst and found that maximum activity was obtained at 500°C with the formation of Cu_yCe_{1-y}O_{2-x} solid solution [40]. These effects are attributed to the CuO–CeO₂ interface, specifically the formation of CeO₂ defects at the CuO–CeO₂ interface and Cu⁺ sites that act as CO adsorption sites. The dual-site mechanism was demonstrated by Ji et al. [41]. They studied model Cu₈ clusters supported on the CeO₂ (111) surface by density functional theory and demonstrated the critical role of oxygen vacancies, which modulate the O₂^{*} intermediate and facilitate the reaction of the adsorbed CO with activated O₂^{*}.

Although the TOF of 0.5wt% Cu/CeO₂ in this study is significantly higher than that reported in most of the other reports, it is still lower than the TOF of the CuCe-Rex catalyst pretreated in 1% CO/Ar at 200 °C for 1 h reported by Tian et al. [34]. Their TOF was 40 × 10⁻² s⁻¹ at 70 °C, which was far higher than that in this study (1.0 × 10⁻² s⁻¹ at 70 °C for 0.5 wt% Cu/CeO₂), as shown in Table S2. This may be because of the difference in the pretreatment because our catalysts were pretreated in 10%O₂/N₂ at 300 °C for 15 min. Comparing the catalyst after oxidation pre-treatment (CuCe-Ox pretreated in 20%O₂/N₂ at 200 °C, the TOF (1.5 × 10⁻² s⁻¹) is almost identical taking higher SV into account. Although there is no information about CuO dispersion in Tian's paper, it can be expected that, in the CuCe-Rex catalyst reported by Tian et al., the reduction treatment resulted in the increase in the contact of Cu with CeO₂ and maximized the activity of Cu–O–Ce sites.

4 Conclusion

Cu/CeO₂ exhibited higher CO oxidation activity than Pt/CeO₂ below 150 °C. Cu/CeO₂ achieved the highest TOF at 0.5 wt%. In this catalyst, CuO is supported in a nanoisland having 1.0 nm diameter, and contribution of the peripheral oxygen of the CuO nanoisland, i.e., Cu–O–Ce sites, was suggested from anaerobic CO oxidation. Previous papers have reported the importance of the interface between CuO and CeO₂ in Cu/CeO₂ catalysts, this finding further clarified the active chemical species of Cu/CeO₂ at the interface.

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Supplementary Information: The online version contains supplementary material available.

Author Contribution Information

Fuka Takahashi: Conceptualization and Verification, Investigation, Data analysis. Takeshi Ohtsu: Conceptualization and Verification, Investigation, Data analysis. Atsushi Satsuma: Writing – review & editing, Funding acquisition and Supervision.

Competing Interest Information

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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